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# ***JPRS Report***

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***Central Eurasia:  
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# Science & Technology

## CENTRAL EURASIA: Chemistry

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11 December 1992

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**Azorhodanines and Their Application to Chemical Analysis**

927M0211A Moscow *ZHURNAL ANALITICHESKOY KHMII* in Russian Jul 92 pp 1157-1182

[Article by R. F. Guryeva, S. B. Savvin, Institute of Geochemistry and Analytic Chemistry imeni V. I. Vernadskiy, Russian Academy of Sciences, Moscow; UDC 543.43]

[Abstract] This review of the Russian literature discusses recent progress in the synthesis, theoretical study and application of new azoreagents based on rhodanine and its analogues for the determination of noble and heavy metals and rhenium. Problems of the synthesis and theoretical study of 5-azosubstituted rhodanine and its analogues thiorhodanine, 3-aminorhodanine, thiohydantoin, pseudothiohydantoin, thiopropiorhodanine, selenizorhodanine and benzene azobenzene azorhodanine derivatives are analyzed. Considerable attention is given to the peculiarities of the interaction of reagents of this class with noble and heavy metals and rhenium and to practical applications. Interaction of the reagents with

many metal ions is described and the reaction conditions and capacity to tolerate the presence of elements are listed in tabular form. Examples of the use of azorhodanines in analysis are tabulated, including photometric, chemical sensor, paper and thin-layer chromatography, differential photometric and kinetic analysis. References 71 Russian.

**Moscow Seminar on Analytical Chemistry**

927M0223G Moscow *ZHURNAL ANALITICHESKOY KHMII* in Russian Vol 47, No 5, May 92 pp 951-952

[Article by G. A. Pribylov]

[Abstract] The title seminar convened on 24 September 1991 with a report "Analytical Control of the RSFSR Environment", by Ye. Ya. Neyman (Moscow). This was followed by three more reports on environmental matters and a report on laser plasma. Other reports were presented on the analysis of rare and noble metals in minerals and industrial products as well as natural and waste waters.

**Electrocatalytic Processes in Alkaline Electrolyzers**

927M0205A Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 3, Mar 92 (manuscript received 15 Mar 91)  
pp 391-397

[Article by S.F. Chernyshov, Yu.I. Kryukov, and A.G. Pshenichnikov, Electrochemistry Institute imeni A.N. Frumkin, Russian Academy of Sciences, Moscow]

[Abstract] The electrochemical characteristics of electrodes activated by surface skeletal catalysts based on nickel and nickel alloys in reactions of the evolution of hydrogen and oxygen in an alkaline electrolyte were examined. The studies performed established that the energy expenditures occurring during the electrolysis of water consist of polarization losses at the electrodes and ohmic losses in the electrolyte and current-carrying conductors. In cells with external perforated electrodes the ohmic losses in the electrolyte account for a third of the total energy losses, which limits the current densities in electrolyzers with that type of design to 2.0-2.5 kA/m<sup>2</sup>. In compact cells with wire-gauze electrodes, the fraction of ohmic losses in the diaphragm is much lower, and energy losses are dictated primarily by the electrodes' basic polarization. The studies conducted also established that activating the electrodes makes it possible to reduce total polarization losses at the cathode and anode by about 0.3 to 0.4 V. The characteristic lengths of processes of hydrogen and oxygen evolution on electrodes with nickel surface skeletal catalysts were determined: Under the conditions studied, the characteristic length of the process of oxygen evolution was found to be about 30  $\mu$ m, which is a factor of 2 to 3 less than the characteristic length of the process of hydrogen evolution. Process temperature was found to be a key factor in increasing the efficiency of oxygen and hydrogen evolution. In the experiments reported herein, efficiency increased by 1.5 to 2 orders of magnitude as the process temperature was increased from 25 to 120° C. The researchers proposed a method of increasing the adhesion strength of electrodes' active catalytic layers so as to keep the electrochemical characteristics of electrolysis cells with activated electrodes stable over time. Having small quantities of NiAl (2 to 5 wt.-%) present in the surface skeletal catalyst was shown to increase the layer's strength significantly and ensure that the activated electrodes would function in a stable manner. In addition, using activated wire-gauze electrodes that were in contact with an asbestos board diaphragm ( $\Delta \approx 3$ -3.5 mm) makes it possible to reduce the voltage in the cell by about 0.4 V versus commercial electrolyzers without altering the current density (i.e., increase the device's productivity by a factor of 3 to 4 without altering the electricity required). Reducing the thickness of the diaphragm to 0.6 mm made it possible to reduce the voltage in the cell by an additional 0.2 to 0.25 V. Figures 7, tables 3; references 17: 8 Russian, 9 Western.

**Autocatalytic Phenomena in the Electroreduction of Ortho- and Para-Isomers of Dicyanobenzene in Dimethyl Sulfoxide Solutions**

927M0205B Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 3, Mar 92 (manuscript received 4 Jun 91)  
pp 441-450

[Article by L.N. Nekrasov, S.M. Peregudova, and L.P. Yuryeva, Moscow State University imeni M.V. Lomonosov and Elementoorganic Compounds Institute imeni A.N. Nesmeyanov, Russian Academy of Sciences, Moscow; UDC 541.138.3]

[Abstract] The autocatalytic phenomena occurring during the electroreduction of *ortho*- and *para*-isomers of dicyanobenzene in dimethyl sulfoxide [DMSO] solutions was examined. All measurements were made on rotary disk and disk-and-ring electrodes made of amalgamated gold. Purified DMSO with a starting water content of 0.05 to 0.1 wt.-% (i.e., a "dewatered" solvent) was used. Tetrabutylammonium tetrafluoroborate was used as the electrolyte, and an aqueous standard calomel electrode was used as the comparison electrode. The researchers plotted the polarization curves of the electroreduction of phthalonitrile in a solution of  $4 \times 10^{-3}$  M phthalonitrile + 0.1 M (C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>NBF<sub>4</sub> in "dewatered" DMSO obtained at three disk electrode rotation speeds. At a rotation speed above 700 rpm, two waves were present in the curve. The first (wave A) corresponded to the reversible transfer of one electron and the formation of phthalonitrile anion radicals. The second (wave B) corresponded to an irreversible total process resulting in the elimination of one cyano group and the formation of a benzonitrile anion radical. The polarization curve in the range of potentials of wave B was found to undergo significant changes when the measurements were made at a comparatively low rotation speed (390 rpm): Wave B split into two waves with very different polarization characteristics. The ratio of the heights of the waves B<sub>1</sub> and B<sub>2</sub> was found to depend on the electrode rotation speed, the potential of the half-wave E<sub>1/2</sub><sup>B1</sup> shifted 0.16 V to the positive direction versus the potential of the half-wave of the nonsplit wave B, and the values of E<sub>1/2</sub><sup>B1</sup> and E<sub>1/2</sub><sup>B2</sup> virtually coincided with one another. In addition, the slope of the wave B<sub>1</sub> decreased sharply (under the study conditions, it amounted to just 0.015-0.020 V). These effects disappeared as the electrode rotation speed increased. The unusually low slope of the wave B<sub>1</sub> (which indicates a strong acceleration of the irreversible process as the electrode's polarization increases) and the disappearance of this effect as electrode rotation speed increases were taken as indications that the electroreduction process is autocatalytic in nature. The process accelerated sharply as the current force and concentration of reaction products near the electrode increased. The quick discharge of the products from the space near the electrodes at high electrode rotation speeds eliminated their catalytic effect on the process. The mechanism of the autocatalytic acceleration of processes of the electroreduction of *ortho*- and *para*-isomers of dicyanobenzene on a gold amalgamated disk electrode in DMSO solutions with small amounts of water was said to be based on the regeneration of the water

that participates in the process as a proton donor. This water is said to cause a Hoffman splitting of the tetrabutylammonium cations in the near-electrode layer of the disk under the effect of the hydroxyl ions formed during the course of the electrode process. Figures 6; references 18: 9 Russian, 9 Western.

**Influence of Aqueous-Organic Solvent Composition on Rate of Photocatalytic Liberation of Hydrogen From Cobalt Cyano-Ethylenediamine Complex Solutions**

927M0208D Moscow *KHIMIYA VYSOKIKH ENERGIY* in Russian Jul-Aug 92 pp 328-332

[Article by N. L. Gololobova, M. B. Rozenkevich; UDC 541.14]

[Abstract] Results are presented from a study of the influence of the composition of aqueous organic solutions of cyano-ethylenediamine cobalt complexes on the rate of photocatalytic extraction of hydrogen. Solutions were prepared by mixing of initial solutions of cobalt chloride hexahydrate, sodium cyanide and double distilled ethylenediamine in a vacuum. Solutions were irradiated with the full light flux of a high pressure mercury lamp in quartz cuvettes with absorption layer thickness 0.5 cm, assuring virtually total absorption of the light at all wavelengths up to 400 nm, the area active for the photocatalytic process. The total light flux was  $3.7\text{--}4.5 \times 10^{-5}$  mol/min. The hydrogen liberation rate was continuously monitored. All experiments were performed at 20° C. A synergic effect was observed in the presence of acetone, with the rate of hydrogen liberation significantly greater than the rate from solutions containing either of the organic additives alone. The article does not explain the effect, but assumes that one cause is that the acetone takes part in the formation not only of the solvate shell of the complex ion, but also its internal coordination sphere. Figures 2; references 14: 9 Russian, 5 Western.

**Characteristics of Granulated Oil Hydrorefining Catalysts**

927M0209A Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian Jun 92 pp 18-20

[Article by N. M. Aliyev, V. S. Aliyev, A. A. Kasimov, I. M. Babayev, Institute of the Petrochemical Industry imeni Yu. G. Mamedaliyev, Azerbaijan Academy of Sciences; UDC 66.015.23.66.097.13]

[Abstract] Hydrorefining of oil distillates is performed with a mixture of liquid and gas raw materials flowing over a granulated catalyst layer. All factors influencing the effectiveness of contact of the liquid with the catalyst depend on the hydrodynamic situation in the catalyst layer, its structure and the characteristics of the catalyst. Although information is available in the literature on the permeability of a liquid in a porous medium, the structure of such media is too complex and varied to allow analysis by a simple model. Predictions must be based on an empirical approach combining the use of theoretical

models and experimental measurement of the physical properties of the catalyst. This article presents a study of industrial  $\text{NiO}(\text{CoO})\text{--MoO}_3\text{--SiO}_2$  catalysts on alumina bases with grain size 4-8 mm, porosity 42%, bulk density 694-829 kg/m<sup>3</sup>. The quantity of gas adsorbed by the catalyst was studied as a function of pressure at constant temperature using nitrogen at relative pressure 0.05-3 at low temperatures, using liquid nitrogen as the cooling agent. The quantity of adsorbed gas corresponding to a monomolecular layer, total pore volume, specific hydrodynamic surface, porosity and bulk density were determined. The hydrodynamic and physical characteristics of the granulated catalysts presented here can serve as a basis for computation of the major heat and mass transfer parameters of a catalyst grain or layer. References 11: 8 Russian, 3 Western.

**Nonethyalted Motor Vehicle Gasoline From Reforming Catalysate**

927M0209B Moscow *KHIMIYA I TEKHOLOGIYA TOPLIV I MASEL* in Russian Jun 92 pp 20-21

[Article by S. M. Moyiseyev, Yu. A. Skipin, Yu. L. Romanovich, N. A. Semenova, Odessa Scientific-Production Plant, "Lennftekhim" Scientific Production Association; UDC 665.733:665.644.442]

[Abstract] An experiment is described involving production of nonethyalted type AI-91 and AI-76 motor vehicle gasoline from reforming catalysate (reformate) at the Odessa oil refinery. In the previous technology, the octane number of the gasoline mixture was increased by ethylation to the level required for the gasoline type desired. After redesign of the secondary distillation installation it became possible to separate the straight-run -85° C fraction into light and heavy parts, differing significantly in knock resistance. This made it possible to use two components to produce gasoline: the relatively high-octane light fraction (octane No. 79) and the low-octane heavy fraction (octane No. 62). Severe reforming can produce a fraction with an octant number of up to 85. Type AI-91 gasoline is produced of this product with the addition of up to 10 percent of the light straight-run fraction, A-76 by mixing a milder reformate with octane No. 80 with up to 35 percent of the heavy straight-run fraction. The results of qualification testing are presented, indicating that the fuels meet the requirements of the specifications. Figure 1.

**Catalymetric Determination of Trace Vanadium in Solutions With Ionometric Reaction Rate Monitoring**

927M0211D Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian May 91 pp 1304-1309

[Article by L. N. Moskvina, D. V. Golikov, Zh. R. Josse, M. F. Grigoryeva, I. V. Kruglova, St. Petersburg State University; UDC 543.43:546.881]

[Abstract] The appearance of ionometric sensors, particularly bromide-selective electrodes, which are stable in



corrosive media, can lead to new analytic methods based on the use of catalytic reactions. This article is dedicated to the development of a catalytic method for determination of vanadium with ionometric recording of changes in the concentration of bromide ions in solution. All measurements were performed in a thermostatic cell with bromide-selective chalcogenide glass electrode. To perform measurements in the cell, an aliquote part of the solution to be analyzed or a solution with a known vanadium concentration was placed in the cell, potassium bromate was added, a mixture of acetic and nitric acids was used to create pH 3. After a steady potential was achieved in the system the corresponding carboxylic acid was added. Catalymetric determination of vanadium is suitable for analysis of waste water, requiring about 30 minutes as opposed to 2.5-3 hours for photometric determination and not being hindered by a 10,000 times excess of alkali and alkali-earth metal ions, cadmium, lead, cobalt, nickel, nitrate and sulfate ions, a 1,000 times excess of ammonium ions, a 150 times excess of iron, copper and chloride ions. Figures 4; references 10: 9 Russian, 1 Western.

#### Reaction Activation Energy in Heterogeneous Catalysis

927M0213A Moscow DOKLADY AKADEMII NAUK SSSR Vol 322, No 4, Jan-Feb 92 (manuscript received 20 Nov 91) pp 744-748

[Article by V. V. Gerasimov, V. V. Gerasimova, and A. G. Samoylov, associate member, Russian Academy of Sciences, Scientific Research and Construction Institute of Energy Technology; UDC 541.124]

[Abstract] The conservation of momentum was used to evaluate the influence of a catalyst on reaction activation energy. For the decomposition of ammonia on tungsten the momentum of a W atom was determined to be  $9 \times 10^{-17}$  g cm/sec, while that of  $\text{NH}_3$  was  $1.5 \times 10^{-18}$  g cm/sec. As a result of the interaction the  $\text{NH}_3$  molecule velocity is  $2.85 \times 10^5$  cm/sec, while the energy of each NH bond increases by 22 kJ/mole. Cleavage of the NH bond increases the N to H distance  $3.81-4.05 \times 10^{-9}$  cm. Total activation energy for cleaving all three NH bonds was calculated to be 134-159.5 kJ/mole, slightly less than the experimental value of 163 kJ/mole. Similar calculations were carried out for the cleavage of ammonia on Mo, Fe, and Os. For the cleavage of methane on platinum the calculated activation energy was 211-249.5 kJ/mole, while the experimental values are 230-252 kJ/mole. The activation energy of the production of  $\text{OH}_2$  from  $\text{nH}_2$  was calculated to be 42.3, 45.1, 42.8, and 33.4 kJ/mole on Ni, Fe, Pt, and Pd; the respective experimental values are 33.4, 43, 35.1, and 20 kJ/mole. In the decomposition of HI the activation energy of the reaction can only be affected by interaction with adsorbed catalyst molecules. Calculated activation energies on Pt and Au were 59 and 101 kJ/mole, while the experimental values are 59 and 105 kJ/mole respectively. For the reaction of  $\text{SO}_2$  with oxygen to produce  $\text{SO}_3$  a Pt catalyst decreases activation energy from 251 kJ/mole to 155.6

kJ/mole. Experimental values for this decrease are 63-92 kJ/mole. The differences between calculated and experimental values were not statistically significant. References 3: Russian.

#### Extraction of Gold Using Crown Ethers and Podands

927M0213B Moscow DOKLADY AKADEMII NAUK SSSR Vol 322, No 4, Jan-Feb 92 (manuscript received 10 Dec 91) pp 740-743

[Article by V. V. Yakshin, O. M. Vilkova, L. T. Makarova, N. A. Tsarenko, and Academician B. N. Laskorin, All-Union Scientific Research Institute of Chemical Technology; UDC 542.61]

[Abstract] The use of linear (podands) and cyclic (crown ethers) polyethers in the recovery of trace amounts of gold from chemically complex chloride containing solutions was investigated. Plasma and gamma spectroscopy were used to measure gold concentrations, which were less than 10 mg/L in the starting solutions. It was found that the concentration of HCl and chloride ions, as well as other impurities in the aqueous phase, the concentration and structure of the extracting agent ether, and the type of organic solvent used all influenced the gold distribution coefficient. This coefficient increased with increasing HCl concentration and with the number of ether oxygens in the extracting agent. Particularly large coefficients were found for the dibutyl ethers of tetraethylene glycol and pentaethylene glycol, since these compounds are capable for forming stable pseudomacrocyclic rings. Since in theory 18-crown-6 ethers should be even better extracting agents, eleven such compounds were tested. Phenyl substituents on the crown ether decreased the gold distribution coefficient, relative to aliphatic substituents, while saturated rings increased extraction. The cyclohexyl substituted crown ethers were the most effective extracting agents. These compounds are recommended for use in hydrometallurgy and analytical chemistry. References 6: 3 Russian, 3 Western.

#### Heterometallic Carbido-carbonyl Clusters as Catalysts of Acetylene Compound Hydroxylation

927M0219A St. Petersburg ZHURNAL OBSHCHEY KHIMII Vol 62(124), No 2, Feb 92 (manuscript received 12 Mar 91) pp 346-351

[Article by L. I. Kopylova, V. B. Pukhnarevich, L. B. Gurevskaya, M. Ts. Tsybenov, and M. G. Voronkov, Irkutsk Institute of Organic Chemistry, Siberian Department, Russian Academy of Sciences; UDC 547.1.128:547.314-517.21]

[Abstract] A study was conducted on the interaction of phenylacetylene with trichloro-, methylchloro-, ethyldichloro-, dimethylchloro-, triethyl-, and triethoxysilanes in the presence of a series of polyheterometallic carbido-carbonyl clusters of a new form, namely

[RhFe<sub>5</sub>C(CO)<sub>16</sub>](CH<sub>3</sub>)<sub>4</sub>N (I), [Rh<sub>2</sub>Fe<sub>4</sub>C(CO)<sub>15</sub>][(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]<sub>2</sub> (II), and [Rh<sub>3</sub>Fe<sub>3</sub>C(CO)<sub>15</sub>](C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N (III). [Rh<sub>5</sub>Fe(CO)<sub>16</sub>](C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N (IV), which does not contain a carbide carbon atom, and H<sub>2</sub>PtCl<sub>6</sub> (V) were used for comparison. Compounds I-III were found to be less powerful catalysts than IV and V. Iron pentacarbonyl did not catalyze the reactions under study. No pronounced dependence of total adduct yield on catalyst structure was noted. This is due to the fact that under oxidative-reductive conditions the six-nuclear complexes I-III are converted to [RhFe<sub>4</sub>C(CO)<sub>14</sub>]<sup>-</sup>, and then to a mixture of five- and six-nuclear clusters. The true catalytic moiety may be "Rh(CO)." The regioselectivity of catalysts I-IV always results in predominance of the β isomer. Reaction stereoselectivity was not strongly dependent on the Si substituent, resulting in essentially equal amounts of cis and trans isomers, except with dimethylchlorosilane, which exhibited high stereoselectivity for the cis isomer. This preference for cis isomer formation distinguished the compounds under study from other rhodium complexes. Increasing reaction temperature from 100° C to 130° C decreased cis isomer content. References 19: 13 Russian, 6 Western.

#### Mild Catalytic Acyldealkylation of Simple Ethers

927M0219B St. Petersburg ZHURNAL OBSHCHEY  
KHIMII Vol 62(124), No 2, Feb 92 (manuscript received  
31 Sep 90) pp 375-378

[Article by N. I. Tyryshkin, A. N. Vedernikov, B. N. Solomonov, and G. G. Garifzyanova, Scientific Research Chemical Institute imeni A. M. Butlerov, Kazanskiy State University imeni V. I. Ulyanov-Lenin; UDC 547.27]

[Abstract] As part of the search for catalysts of ether bond cleavage under mild conditions, ten transition metal salt catalysts were tested using the reaction of methylal (dimethoxymethane) with acetic anhydride in acetonitrile, at 20° C for 24 hours. Complete conversion into methyl and methoxyacetates was obtained with FeCl<sub>2</sub> and FeCl<sub>3</sub> 6 H<sub>2</sub>O. Intermediate conversion rates observed with other catalysts tested were 60% with CeCl<sub>3</sub>, 50% with CoCl<sub>2</sub> 6 H<sub>2</sub>O, 40% with CoCl<sub>2</sub>, and 10% with AlCl<sub>3</sub>. No reaction was obtained with NiCl<sub>2</sub>, Co(NO<sub>3</sub>)<sub>2</sub> 6 H<sub>2</sub>O, CoCl<sub>2</sub> + PPh<sub>3</sub>, and SmCl<sub>3</sub>. Analogous results were obtained with other acetals. 9-Methoxyfluorene, Ph<sub>2</sub>CHOMe, PhMeCHOMe, MeOPhCH<sub>2</sub>OMe, MeOPhCH<sub>2</sub>OPh, BuOBu, and PrOPr were tested with CoCl<sub>2</sub> in argon and air, and with CeCl<sub>3</sub>,

FeCl<sub>2</sub> and FeCl<sub>3</sub> 6 H<sub>2</sub>O. Conversion rates from 10% to 100% were noted. The products were 85%-95% acetates using the first three catalysts, but only 40%-60% using the last. The results suggest that the reaction proceeds via single electron transfer. The reaction probably occurs in the metal coordination sphere, as indicated by its complete inhibition by triphenylphosphine. References 12: 2 Russian, 10 Western.

#### Electrochemical Azidation of Aniline

927M0219C St. Petersburg ZHURNAL OBSHCHEY  
KHIMII Vol 62(124), No 2, Feb 92 (manuscript received  
23 Jul 90) pp 406-410

[Article by V. G. Koshechko, S. A. Shpilnyy, and V. D. Pokhodenko, Institute of Physical Chemistry imeni L. V. Pisarzhevskiy, Ukraine Academy of Sciences, Kiev; UDC 541.138.2+547.551]

[Abstract] The first investigation of the possibility of obtaining aniline azide derivatives via a one-stage electrochemical anode replacement of hydrogen in the aromatic nucleus is reported. The cyclic voltamperogram of N,N-dimethylaniline oxidation indicates that an unstable cation-radical is produced, which subsequently dimerizes. In contrast, aniline produces a nonreversible wave. The oxidation of the azide ion proceeds with more difficulty than the oxidation of either aniline or N,N-dimethylaniline. When measuring the voltampere curve of a methanol solution containing both dimethylaniline and sodium azide, a sharp increase in the oxidative current of the former was observed, while the peaks in the cathodic portion of the curve attributed to reduction of the cation-radical and the dimer disappeared. Similar increases in oxidative current were noted with aniline and sodium azide, accompanied by the disappearance of the cathodic peak assigned to the reduction of azobenzene. The IR spectra of the products of preparative electrolysis contained peaks corresponding to the symmetric and asymmetric oscillations of an azide group bonded to an aromatic nucleus. The NMR spectra of the products contained three or four signals corresponding to a π-azidoaniline, as well as a signal for π-quinonediimine, its photolysis product. For N,N-dimethylaniline, the NMR spectrum indicated that the azide was para to the methyl groups. Yields in methanol were 52% for aniline and 81% for dimethylaniline. Water and acetonitrile gave lower yields. A mechanism for the reactions is proposed. Figures 2; references 12: 5 Russian, 7 Western.

**Influence of Surface-Active Substances on Colloidal Structure of Oil Distillates**

927M0209C Moscow *KHIMIYA I TEKHNLOGIYA TOPLIV I MASEL* in Russian Jun 92 pp 29-30

[Article by Ch. Kh. Sagitova, R. G. Yaushev, R. Z. Safiyeva, Bashkir State University, GANG imeni I. M. Gubkin; UDC 665.662.3]

[Abstract] A study is presented of the mechanism of the influence of surfactants on redistribution of hydrocarbons in the process of phenyl refining of oil fractions. The 350-420° C fraction was studied of a mixture of Tuymazy and western Siberian petroleum (ratio 1:2). The method of investigation involved measurement of the amplitude and time delay of current flowing through a specimen exposed to a sine wave voltage of up to 10 V at 20-10<sup>5</sup> Hz and temperatures 30-80° C. The real and imaginary parts of the complex dielectric permeability were then computed. The variation of dielectric parameters as calculated by the Debye equation were studied for the distillate specimens. It was found that the independent kinetic units in the process of dipolar polarization are associates including most of the molecules of the polar components of the system. The relaxation time of the associates is determined by their size and the polarity of their component molecules. The maximum relaxation time is that of a distillate with 0.005% PMS-200A surfactant by mass, decreasing significantly with increasing temperature as a result of the reduced viscosity of the dispersed system. The concentration of 0.005% is the critical concentration for micelle formation in the distillate studied. The redistribution of hydrocarbons and heteroorganic compounds between the dispersed phase and dispersion medium with the surfactant present changes the relaxation time of dipole polarization of the associates. Figures 4; references 4 Russian.

**Influence of Colloid-Chemical Properties of Fluoroorganic Latexes on Modification Effectiveness of Fiber Materials**

927M0210D Moscow *KHIMICHESKIYE VOLOKNA* in Russian May-Jun 92 pp 37-38

[Article by L. S. Sletkina, N. V. Kolokolkina, L. V. Redina and O. K. Antonova, Moscow State Textile Academy; UDC 677.463-96.014.8]

[Abstract] Using latexes of polymers and copolymers of fluoroalkylacrylates presently used to reduce the wettability of fibers and give materials based on them water-acid- and oil-repelling properties, the authors demonstrate the influence of some of their colloid-chemical characteristics on these properties. Latexes were produced by water-emulsion polymerization of monomers in various surfactants. The chemical fibers were treated by wetting in dilute latex, pressing, drying and heat treatment at 413-423 K for several minutes. Wettability of the modified fibers was determined by measuring the contact wetting angle with glycerin or water and by measuring oil-repellant properties by the 3M method, based on measurement of the wetting capability of a mixture of vaseline oil and n-heptane at various ratios. It was found that the effectiveness of using various types of latex fiber with small particle diameter is higher under the same conditions. This is because the smaller particles of latex, with the identical quantity of stabilizer, have a less saturated adsorption layer, facilitating heterocoagulation and apparently easing the formation of a more uniform polymer layer on the fiber. In developing a technology for using such systems it must be recalled that their aggregate stability decreases with decreasing saturation of the adsorption layers. References 6: 5 Russian, 1 Western.

**A Voltammetric Study of Electrode Processes in Acetate Solutions on a Platinum Electrode**

927M0201 Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 2, Feb 92 (manuscript received  
5 Apr 90) pp 158-164

[Article by Sh.Sh. Khidirov, Dagestan State University  
imeni V.I. Lenin, Makhachkala; UDC 541.138.2:547]

[Abstract] The author used the method of recording voltammetric curves to study the electrochemical oxidation of an acetate ion on a platinum electrode in an alkaline medium within a wide range of anode potentials. A P-58 27 M potentiostat was used to record the voltammetric curves, and an LKD 4-003 potentiometer with automatic recording was used to record the polarization current and potential of the working electrode. A platinum wire soldered into glass served as the working electrode; it had a geometric surface of 0.13 cm<sup>2</sup>. The auxiliary electrode was also made of platinum. The working electrode's potential was measured relative to a hydrogen electrode in the same solution. Two oxidation waves in the potential intervals from 2.2 to 2.3 V and 3.2 to 3.3 V were found in the voltammograms recorded in the alkaline sodium acetate solutions. The first oxidation wave corresponded to the discharge of water molecules or hydroxide ions, whereas the second wave corresponded to the discharge of acetate ions. The acetate ion and hydroxide ion concentrations had qualitative and quantitative effects on both oxidation waves: The qualitative effect was reflected in the different degrees of distinctness of the oxidation maxima, and the quantitative effect was reflected in the change in the ratio of the waves' currents. The curves recorded in a concentrated sodium acetate solution containing 0.1 M sodium hydroxide contained an additional current delay in the potential range from 2.6 to 2.8 V. It was hypothesized that this wave is the result of a new type of electrode reaction. Figures 4; references 8: 5 Russian, 3 Western.

**The Electrochemical Behavior of a Solid Li<sub>3</sub> Electrolyte Under a Current**

927M0201C Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 2, Feb 92 (manuscript received  
14 May 91) pp 232-240

[Article by O.V. Zhelmonozhko, V.P. Obrosof, and N.N. Batalov, Electrochemistry Institute, Ural Department, Russian Academy of Sciences, Yekaterinburg; UDC 531.135.5]

[Abstract] An examination was made of the stability of the electrical properties of solid lithium nitride after a direct current of elevated density had been passed through it at a temperature of 300° C. Lithium nitride was selected as a model electrolyte for the study because it is a highly conductive cationic conductor that does not react with lithium. The cell used consisted of a lithium nitride tablet measuring 10 mm in diameter and 5 mm in thickness. The density of the nitride tables in the individual experiments ranged from 96.0 to 99.5% of the theoretical density. During the experiments the cell was heated to 300° C in an atmosphere of

purified helium. A current with a density of 0.65 A/cm<sup>2</sup> was passed through it in a galvanostatic mode. The oxygen pressure in the cell was measured by a sensor and kept close to 1.62 x 10<sup>-10</sup> Pa. The experiments performed established that the resistance of the electrolyte under a current changes over time in accordance with a complex law even in the absence of any decomposition of the electrolyte. After the current was switched on, the cell's resistance dropped from 3.8 to 3.0 ohms and then slowly rose to 6.5-7.5 ohms. The initial drop in the cell's resistance was attributed to the removal of the electrode's surface films under the current. The next phase of the cell's behavior, i.e., the marked increase in resistance, was left unexplained owing to the need for further studies. When the study specimen was cooled to room temperature, the electronic nature of its conduction became very evident. Microscopic lithium inclusions that were not related to contact with the electrodes appeared in the volume of the electrolyte. A deviation from stoichiometric in the cation sublattice coupled with the appearance of the respective electron carriers in its zones was offered as one possible reason for the degradation of the electrolyte. The researchers used the method of coulometric titration to test this hypothesis. The data collected from the coulometric titration indicated a narrow region of homogeneity in lithium nitride that is caused by small deviations from stoichiometry in the cation sublattice during equilibrium with metallic lithium. At 400° C the solubility of lithium in nitride is on the order of 0.01 at.-%. In the starting nitride produced under a nitrogen pressure on the order of 1 atm there is a shortage of lithium cations that is compensated for either by the appearance of electron holes or else by impurities in the anion sublattice that have a different valence. At 400° the contribution of electron conduction reaches 70 to 75% of the nitride's total conduction. The carriers were found to have an effective mass of 0.285m<sub>0</sub>. The Fermi level in lithium nitride in equilibrium with lithium was found to lie close to the bottom of the conduction zone, which indicates the high likelihood of electrical and mechanical degradation of the electrolyte under a current on account of the separation of lithium in the structural inhomogeneities of the material. The voltage of the decomposition of lithium nitride as determined by electrochemical methods was found to be far above that calculated from the thermodynamic data presented: At 400° C it equals at least 1.208 V. Figures 6, table 1; references 12: 5 Russian, 7 Western.

**A New Method of Describing Mass Transfer During an Electrochemical Reaction at the Bottom of a Cylindrical Channel**

927M0201D Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 2, Feb 92 (manuscript received  
1 Jul 91) pp 251-264

[Article by G.R. Engelhardt, A.D. Davydov, T.B. Zhukova, and Kh.-Kh. Shtreblor, Electrochemistry Institute imeni A.N. Frumkin, Russian Academy of Sciences, Moscow, and Physical Chemistry and Electrochemistry Institute, Dusseldorf; UDC 541.138.2]

[Abstract] A new method was developed of describing the ion transfer processes that occur during an electrochemical reaction on an electrode that is the bottom of a cylindrical channel in a dielectric material. The method is designed for use with an arbitrary ratio between the channel's depth ( $l$ ) and radius ( $a$ ). In order to be able to consider the phenomenon of mass transfer in a real region representing a cylinder with an adjacent half-space, the authors examined the case of transfer in a cylinder with a depth of  $l + 0.817a$ . The method developed is approximate in nature and is based on the selection of some formal parameter  $\Delta_2$  that depends solely on the channel radius and that permits a theoretical calculation of the reaction rate. The new method makes it possible to give consideration to the fact that the ion concentrations in some external region beyond the confines of the cylindrical region are different from the volumetric concentrations. The essence of the new approximate method (which reduces the problem to a one-dimensional problem) lies in the fact that mass transfer is examined in a channel with a radius of  $a$  (as is usually the case) but that has a depth of  $l + \Delta$  (as opposed to just  $l$  in the existing approach to the problem). The value of  $\Delta$  is selected such that the resistance of an electrolyte column with a height of  $\Delta$  equals the resistance of the specified external region. A concrete expression for calculating  $\Delta_2$  is presented. The authors provide a substantiation of their method and a series of sample calculations. They then compare the results of calculations made by using their new method with the results of an actual experiment. Different degrees of consistency between the calculated and actual experimental results were achieved depending on the individual parameters involved (including electrode radius and chemical composition of the electrolyte solution). The proposed method makes it possible to calculate the distribution of concentrations of all types of ions and potentials averaged throughout the channel's cross section and the current density in the channel under different electrochemical process conditions. The results of the work reported herein are said to be applicable in describing those electrochemical processes occurring on an electrode that is the bottom of a cylindrical channel that are typically solved within the framework of the Nernst model by formally replacing the thickness of the Nernst diffusion layer  $\delta$  with  $l + \Delta$ . Unlike the Nernst model, the method proposed herein makes it possible to calculate  $\delta$ . Figures 8; references 21: 11 Russian, 10 Western.

#### Dependence of Surface Charge on the Potential at an Oxide-Electrolyte Interface

927M0203A Moscow ELEKTROKHIMIYA in Russian Vol 28 No 1, Jan 92 (manuscript received 1 Dec 89; after revision 4 Dec 90) pp 14-20

[Article by I.G. Gorichev and V.V. Batrakov, Moscow State Pedagogical Institute imeni V.I. Lenin; UDC 541.135.5]

[Abstract] The authors worked to find a general analytical expression describing the dependence of surface charge on

the potential at an oxide-electrolyte interface. They began their investigation by proceeding from the principles of model ideas regarding the structure of a binary electrical layer developed in the theory of coupled sites. An expression is derived that makes it possible to calculate charge based on the magnitude of the potential jump at the oxide-electrolyte interface ( $E_0$ ) within a broad range of electrolyte concentrations ( $c$ ), pH levels, and values of  $E_0$ . The following parameters must be known in order to perform the calculations:  $N_s$ ,  $k_3^0/k_1^0$ ,  $2[H_0^+]/k_3^0$ , and  $K_{01}$  (where  $k_3^0$  and  $k_1^0$  are two of four adsorption-equilibrium constants that determine the charge of the oxide surface and the ionic portion of the binary layer;  $N_s$  represents the total number of absorption centers;  $K_{01}$  represents the integral capacity of the binary electric layer between the surface of the oxide and the internal Helmholtz plane; and  $[H_0^+]$  is the concentration of hydrogen ions in the volume of the solution at a specified pH ( $pH_{T.N.E.}$  [not further identified])). The results of calculations made by using the new acid-base model were compared with the results of an actual experiment for magnetite in a  $KNO_3$  background solution. A good correlation was found between the two sets of results. The advantage of the dependence derived herein lies in the fact that the cumbersome computer program generally required for similar calculations may be replaced by a relatively simple equation. For the oxides studied, the values of  $[H_0^+]/k_3^0$ ,  $k_1^0$ ,  $k_3^0$ , and  $N_s$  used in the newly derived equations do not depend on the nature of the oxide. Instead, they are all identically linearly dependent on  $pH_0$ , and it is the concentration of the electrolyte that has the main effect on their values. Figures 2, table 1; references 14: 3 Russian, 11 Western.

#### A Spectroelectrochemical Study of Electrodes Coated With Berlin Blue

927M0203B Moscow ELEKTROKHIMIYA in Russian Vol 28 No 1, Jan 92 (manuscript received 2 Apr 91) pp 74-80

[Article by V.V. Kondratyev, I.A. Vinokurov, V.V. Bertsev, S.Ya. Khaykin, and O.M. Zelenina, Leningrad State University; UDC 541.135.5]

[Abstract] The two infrared spectroscopy techniques (diffuse reflection and frustrated total internal reflection infrared spectroscopy) were used in conjunction with electrochemical measurements to study the role that the anions (chloride, sulfate, nitrate) of an electrolyte play in redox processes in Berlin blue films and in determining the degree of oxidation and reduction that such films undergo. The Berlin blue films were synthesized electrochemically under galvanostatic conditions on a platinum substrate from solutions of  $2 \times 10^{-2}$  M Fe (III) and  $2 \times 10^{-2}$  M  $K_3Fe(CN)_6$  acidified to a pH of 1.5 by the acids HCl,  $NH_4OH$ , or  $H_2SO_4$ . When a cathode current of 0.2 to 0.3 mA/cm<sup>2</sup> was used, the total quantity of electricity passed through ranged from 200 to 600 mC/cm<sup>2</sup>. The degree of oxidation experienced by the film was measured at a specified potential in a background electrolyte with a pH of 2. The studies performed established that the anions of the electrolyte do not participate in the film oxidation processes as oppositely charged ions compensating for the film's charge. Complete

oxidation of the thin layer close to the electrode was not found to occur even at a potential of 1.2 V even though the potential of the film's reversible oxidation was close to 0.9 V. The degree of oxidation of Berlin blue films found from the spectra of diffuse reflection under conditions of penetration of a light beam through the films' entire depths was found to be between 20 and 25% at an electrode potential of about 1.1 V. These results were explained by their low conductivity. Figures 4; references 12: 3 Russian, 9 Western.

### Electrical Fields of High-Voltage Electrochemical Circuits in a Conductive Medium

927M0203C Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 1, Jan 92 (manuscript received  
11 Apr 91) pp 89-92

[Article by N.D. Koshel and A.S. Plashenko; UDC 621.355.004]

[Abstract] A numerical solution to the problem of the distribution of potentials and currents in high-voltage circuits of electrochemical devices were explored. Specifically, the authors perform a series of computer calculations to find the two-dimensional electrical fields of high-voltage electrochemical circuits in a continuous conductive medium and in systems with shunting collectors with large cross sections. The calculations performed established that the distribution of a discrete electrical field in a circuit of series-connected electrochemical cells shunted by a continuous conductive medium is analogous to the distribution existing in a conventional one-dimensional circuit with a nonlinear distribution of collector resistances along its length and that the two-dimensional fields under consideration may be adequately represented as a field generated by a system with a one-dimensional nonuniform collector in which the local nodes are specified functions of the coordinate. This function may be determined exactly from the results of a numerical solution based on a two-dimensional model. If the parameters of the said function are known, simple and fast algorithms may be used to solve uniform problems with nonuniform electrical circuits to calculate much more complex systems with two-dimensional collectors. Figures 3; references 6: 4 Russian, 2 Western.

### The Photoelectrochemical Properties of Titanium-Manganese Alloys

927M0203D Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 1, Jan 92 (manuscript received  
19 Apr 91) pp 93-97

[Article by Men Syan Fa, Z.A. Rotenberg, and T.R. Agladze, Senkhua University, Peking; Electrochemistry Institute imeni A.N. Frumkin, Russian Academy of Sciences, Moscow; and Georgia Technological University, Tbilisi; UDC 541.14]

[Abstract] The photoelectrochemical properties of two titanium-manganese alloys containing 8 and 14% manganese, respectively were examined. The electrochemical measurements were made in 0.1 and 1 N H<sub>2</sub>SO<sub>4</sub> with a silver

chloride normal electrode. A potentiostat with a PI-50-1 programmer, Unipan 233 selective nanovoltmeter (Poland), UPI-1 synchrodetector, and two-coordinate potentiometer were used. The intensity of the luminous flux falling upon the electrode was varied periodically at a frequency of 2 to 40 Hz. The electrodes were manufactured in the form of disks measuring 8 mm in diameter. Before each measurement, the electrode was subjected to etching in a 1:1:2 mixture of hydrofluoric, acetic, and nitric acids. The behavior of the study titanium-manganese alloys was also compared with that of pure titanium in sulfuric acid. The dependence of the real component of the photoelectric current  $Re(j)$  and its phase ( $\psi$ ) on potential ( $E$ ) was plotted for pure titanium and for the alloy Ti-Mn (14%). The two dependences turned out to be very different from one another. When  $E > 0.5$  V, the photoelectric current on the alloy Ti-Mn (14%) was much lower than that on the pure titanium. The curves plotted for the Ti-Mn (14%) in forward and backward directions of the change in potential differed more from one another than did the two curves plotted for pure titanium. Only when  $E > 1.5$  V did they nearly coincide. The volt-ampere characteristic of the photoelectric current in the case of the alloy Ti-Mn (8%) was closer to that found for pure titanium. At positive potentials, the photoelectric current on the alloy Ti-Mn (8%) is higher than that recorded on Ti-Mn (14%) but lower than that recorded on pure titanium, and the hysteresis is less pronounced. The hysteresis of the photoelectric current that is characteristic of titanium-manganese alloys is less pronounced when the amplitude of the change in potential is changed from 1.6 V to the negative side. It is in this hysteresis region that the phase shift between the photoelectric current and intensity of the light is observed. It is also the place where the amplitude of the photoelectric current changes as the modulation frequency changes (the amplitude increases as the frequency increases). The positive phase shift between the photoelectric current and intensity of the light found for the titanium-manganese alloys was not found for pure titanium. These differences between the behavior of the titanium-manganese alloys studied and pure titanium were attributed to the photooxidation of manganese and the cathodic reduction of its oxides, as well as to the dark oxidation of manganese. Figures 6; references 9: 3 Russian, 6 Western.

### Low-Temperature Voltammetry and Ultramicroelectrodes in a Study of the Mechanism of Electrochemical Reactions of Organometallic and Organic Compounds

927M0204A Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 4, Apr 92 (manuscript received  
13 May 91) pp 490-497

[Article by V.V. Strelets; UDC 541.13:128:541.135.5]

[Abstract] The methods of low-temperature voltammetry and ultramicroelectrodes have several important advantages when used in studying the mechanism of electrode reactions that entail the formation of unstable intermediate and end products and when studying the redox properties of compounds that are difficult to reduce (oxidize). Ultramicroelectrodes, which is to say

electrodes with linear dimensions ranging from tenths of a micron to several tenths of a micron, are especially promising as research tools. Thanks to the low and ultralow currents that may be recorded when ultramicroelectrodes are used, ohmic (resistance) losses are negligible, and there is thus no longer a need to work with a three-electrode scheme involving the use of a potentiostat. Rather, it becomes possible to use a simpler two-electrode scheme with a sweep generator and micro-, nano-, or picoammeter. The technique of low-temperature voltammetry is a modification of cyclic voltammetry that makes it possible to study reactions at temperatures of  $-100^{\circ}\text{C}$  or lower. Specifically, it is possible to work with tetrahydrofuran and  $\text{CH}_2\text{Cl}_2$  at  $-100^{\circ}\text{C}$ , alcohols and butyrolactone at  $-110^{\circ}$ , ethers at  $-130^{\circ}\text{C}$ , and butyrolactone-ethylchloride mixtures at  $-180^{\circ}\text{C}$ , which is to say with electrodes made of a superconducting ceramic that are in a state of superconductivity. The author of this article has demonstrated the possibilities offered by the method of low-temperature voltammetry with ultramicroelectrodes by way of the examples of electrode reactions of the reduction of benzene and the oxidation and reduction of sandwich and wedge-sandwich complexes of transition metals. The benefits of low-temperature voltammetry and ultramicroelectrodes in studying the reactivity of electrically generated 19-electron systems are also illustrated (specifically, in the study of electron transfer-induced  $\eta^5\eta^6$ -haptotropic regrouping of dibenzoferrrocene). The details of a low-temperature experiment are discussed briefly. Particular emphasis is placed on the stringent requirements regarding the purity of the solvent and the need to use a cell that is a reasonable compromise between vacuum technology and electrochemistry. Figures 3; references 43: 16 Russian, 27 Western.

#### **Electrochemical Initiation of Ion-Radical Reactions of Polyfluoroalkyl Halides. The Production of Perfluorocarbonic Acids**

*927M0204B Moscow ELEKTROKHIMIYA in Russian Vol 28 No 4, Apr 92 (manuscript received 10 Jul 91) pp 498-501*

[Article by N.V. Ignatyev, S.D. Datsenko, and L.M. Yagupolskiy, Organic Chemistry Institute, Ukraine Academy of Sciences, Kiev; UDC 541.138.3:547]

[Abstract] The electrochemical reduction of oxygen in the presence of perfluoroalkylhalides in polar aprotic solvents was examined. The study perfluoroalkyl iodides and bromides were synthesized in Hundiecker's reaction, and the 1,1,1-trifluoro-2,2,2-trichloroethane was produced by isomerization of 1,1,2-trifluoro-1,2,2-trichloroethane by boiling of aluminum chloride. The solvents acetonitrile and dimethyl sulfoxide were purified as described elsewhere, and the oxygen was used without any additional purification. The ammonium tetrafluoroborate used as the background electrolyte was produced as described elsewhere, and the tetrabutylammonium bromide and triethylbenzylammonium chloride were produced by recrystallization from isopropanol. A PI-50-1 potentiostat and

PR-8 programmer were used to record cyclic voltammograms.  $^{19}\text{F}$  NMR spectra were recorded on a Bruker WP-200 spectrometer relative to  $\text{CFCl}_3$ . A quantity of  $100\text{ cm}^3$  of a 0.2 M solution of triethylbenzyl ammonium chloride in dimethyl formamide was poured into the electrochemical cell. Oxygen was bubbled through for 15 minutes, after which 0.01 mole of perfluoroalkyl halide was added. The potential of the working electrode was maintained at  $-0.9\text{ V}$  (normal calomel electrode) during the electrolysis of the reaction mixture. At the end of the electrolysis (after 0.025 F of electricity had been passed through), the dimethyl formamide was evaporated out, and the residue was dissolved in sulfuric acid and extracted by methylene chloride. The extract was rinsed, and the residue was recrystallized from acetonitrile. Cyclic voltammetry was then performed to estimate the reactivity of the perfluoroalkyl halides with respect to the oxygen anion radical. The studies performed confirmed that preparative reduction of oxygen in the presence of perfluoroalkyl halides did indeed result in the respective perfluorocarbonic acids containing two fewer fluorine atoms than the starting perfluoroalkyl halides. An eight-stage diagram of the reaction was developed. According to the diagram, the oxygen acts first as a mediator in stages 1 through 3 and then as a reagent in stages 4 through 8. Figures 4, table 1; references 12: 8 Russian, 4 Western.

#### **The Electrochemical Synthesis of N-Chlorosuccinimide**

*927M0204C Moscow ELEKTROKHIMIYA in Russian Vol 28 No 4, Apr 92 (manuscript received 13 Nov 91) pp 523-526*

[Article by V.A. Petrosyan, B.V. Lyalin, and S.D. Shamshinov, Organic Chemistry Institute imeni N.D. Zelinskiy, Russian Academy of Sciences, Moscow; UDC 541.138+542.944:547.461.4]

[Abstract] In a previous publication, the authors of the present study developed a convenient method for the electrochemical synthesis of N-chloroamines under conditions of diaphragm and diaphragmless electrolysis (yield,  $>90\%$ ). In the present communication, they have reported the electrochemical synthesis of N-chlorosuccinimide. The electrochlorination of succinimide was conducted in a glass vessel (volume, 500 ml) that was located in an ice bath. A two-blade mechanical mixture was used to stir the mixture intensively. Two plane electrodes (surface,  $13\text{ cm}^2$ ) were placed a distance of 2 to 3 mm apart from one another. A VSA-10 rectifier was used as a current source. A coulometer designed by the Special Design Office of the Organic Chemistry Institute of the USSR Academy of Sciences was included in the electric circuit. The content of N-chlorosuccinimide in the end product was determined iodometrically. A quantity of 7.43 g (0.075 mole) succinimide was placed in the electrolyzer along with 150 ml of a saturated aqueous solution of NaCl and 0.6 g  $\text{CaCl}_2$ . An ORTA plate was used as the anode, and a titanium plate was used as the cathode. The electrolysis was conducted with a current of 4.7 A at a temperature of  $10^{\circ}$



C. A quantity of 7.2 ml (0.075 mole) HCl was added to the electrolyte during the electrolysis process. After 2 F electricity per mole of succinimide ( $Q = 1,447$  coulombs) had been passed through the cell, the electrolysis process was halted. The reaction mixture was stirred for an additional half-hour and cooled to 0-2° C. The precipitate was filtered off, resulting in 6.324 g of dry product. According to the iodometric analysis performed, the total yield of N-chlorosuccinimide in the filtrate and precipitate amounted to 80%. The precipitate was rinsed in ice water and vacuum-dried. A quantity of 3.21 g of product containing 93% basic substance with a melting point of 149° C was obtained. A procedure was also developed for using spent NaCl solutions in the electrochemical synthesis of N-chlorosuccinimide. Tables 2; references 6: 3 Russian, 3 Western.

### The Electrochemical Synthesis of Chemicals for Polymeric Materials

927M0204D Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 4, Apr 92 (manuscript received 12 Sep 91)  
pp 540-545

[Article by A.B. Kilimnik, B.N. Gorbunov, and L.G. Feoktistov, Tambov Chemical Machine Building Institute, Tambov; Chemicals for Polymeric Materials Scientific Research Institute, Tambov; and Electrochemistry Institute imeni A.N. Frumkin, Russian Academy of Sciences, Moscow; UDC 541.138]

[Abstract] The sulfenamides N-morpholyl-2-mercaptobenzothiazole and cyclohexyl-2-mercaptobenzothiazolylamine, the vulcanization accelerator Altax, and the light stabilizer 2-(2'-hydroxy-5'-methylphenyl)benzotriazole are presently all produced by oxidation condensation of the respective amines with 2-mercaptobenzothiazole and with sodium hypochlorite as the oxidizing agent. The main drawback of this method is the formation of a large amount of mineral salt solutions that are contaminated with organic substances. The new chemical methods that have been developed to synthesize the above compounds are also fraught with a number of problems related to procuring and storing hydrogen peroxide and pure hydrogen. In an effort to overcome these problems, the authors of the study reported herein worked to develop processes for the electrochemical synthesis of N-morpholyl-2-mercaptobenzothiazole, cyclohexyl-2-mercaptobenzothiazolylamine, Altax, 2-(2'-hydroxy-5'-methylphenyl)benzotriazole, and the latter's N-oxide. Specifically, they performed a series of adsorption, galvanostatic, and voltammetry studies to determine suitable conditions for synthesizing the above four compounds. Their studies enabled them to develop a process flow for the electrochemical synthesis of the sulfenamides N-morpholyl-2-mercaptobenzothiazole and cyclohexyl-2-mercaptobenzothiazolylamine. The process flow includes the following stages: preparation of the electrolyte, electrochemical synthesis, filtration of the hot solution, separation of the sulfenamide from the electrolyte by crystallization by cooling or dilution with water, filtration,

rinsing the sulfenamide with water, drying the sulfenamide, correcting the electrolyte returned from the crystallization separation state, and removing the morpholine and sodium hydroxide from the rinse waters. A test of the process flow in a unit with nickel electrodes (unit capacity, 2,000 kg/y) resulted in a current efficiency of 80% and a product yield of 95%. The resultant sulfenamides were light in color: The N-morpholyl-2-mercaptobenzothiazole and cyclohexyl-2-mercaptobenzothiazolylamine produced had melting points of not less than 83 and 98° C, respectively. A procedure and unit were developed for the electrochemical synthesis of Altax. Tests of the new method and unit established that the best results are achieved when the Altax is synthesized in a saturated solution of sodium 2-mercaptobenzothiozolate at temperatures of 60 to 70° C with an electrolyte pumping rate of 50 to 100 ml/min and current density of 9,000 to 10,000 A/m<sup>2</sup> on platinum electrodes. When these conditions were adhered to, a current efficiency of 80% and product yield of 95% were achieved. The studies of the electrochemical synthesis of 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and its N-oxide established that the best results are achieved in solutions containing methanol, ethanol, or propanol-2 on copper, brass, and steel cathodes with intensive stirring of the solution. The potential must be kept between -1.2 and -1.6 V to obtain 2-(2'-hydroxy-5'-methylphenyl)benzotriazole and between -0.8 and -1.1 V to obtain its N-oxide. The process developed resulted in a product yield of 90 to 95% and a current efficiency of 70 to 75%. References 12: 10 Russian, 2 Western.

### Electrochemical Reactions of Heteroorganic Compounds

927M0204E Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 4, Apr 92 (manuscript received 12 Sep 91)  
pp 615-628

[Article by Yu.M. Kargin, V.V. Zhuykov, Yu.G. Budnikova, and D.S. Fammakhova, Kazan State University imeni V.I. Ulyanov-Lenin and Organic and Physical Chemistry Institute imeni A.Ye. Arbuzov, Kazan; UDC 541.138+541.135.5]

[Abstract] An attempt was made to analyze and summarize the most promising new directions in research on electrochemical reactions of heteroorganic compounds. The first half of the review is devoted to electron transfer-initiated splitting processes. The main conclusion of the section on the electrooxidation of aromatic selenides is that all such processes share a common feature, i.e., a fragmentation reaction initiated by electron transfer. The cathode reduction of ethynyl thio-, seleno-, and telluroethers is said to occur in accordance with an ECE-mechanism and to include the formation of primary anion radicals that undergo potential-dictating fragmentation at the E-C<sub>sp</sub> bond. The fragmentation of cation radicals is said to occur at E-C<sub>sp</sub> or C-H bonds. The former route is more characteristic for organoselenium compounds. This fragmentation has been said to be heterolytic in nature, but the question still remains



open. In the section on the electroreduction of aromatic selenides, the anodic oxidation of alkylarylselenides is said to represent a classical ECE-process. The contributions of the different fragmentation routes, depending on the nature of the substituents in the selenoanisole ring and conditions of the given experiment, as well as the nature of the alkyl group in the alkylphenylselenides' molecules, are said to be easily traced by the change in yields of the respective diselenides. The main conclusion of the section on the electrooxidation of hetero- and homodielement compounds is that the process occurs in accordance with an ECEC-mechanism. The section on the reduction of heteroorganic halogen derivatives includes information on the reduction of chlorosilanes, the reduction of diorganylphosphinites, and the use of the technique of electrochemical reduction of compounds with an E-Hal bond by zero-valent metal complexes as a way of implementing processes of cross-combination with different organic and heteroorganic substrates. The second half of the review is devoted to processes associated with disproportionation and dimerization reactions. The electrooxidation of sulfides and selenides of the aromatic series, the electrooxidation of dielement compounds, and the dual reactivity of heteroorganic intermediates are examined. The main conclusion of this section is that second-order reactions are characteristic for relatively stable heteroorganic cation radicals, with radical properties playing a bigger role than electrophilic properties. Such intermediates are said to disproportionate with the formation of a more reactive electrophilic di-cation and regeneration of the starting molecule. In a number of cases, the orbital-controlled interaction of the cation radicals may be resolved by dimerization. The cation radicals of aromatic heteroethers are said to usually undergo disproportionation, while dielement compounds usually dimerize. Dual reaction is said to be manifested only in processes involving the participation of ion radical intermediates with different potential-dictating interactions having comparable rates. For this reason, a change in the ratio of the ion and radical properties of the intermediates due to the effect of other factors will also be reflected in a change in the nature of the reaction. Tables 6; references 24: 17 Russian, 7 Western.

### The Electrochemical Synthesis of Polymers

927M0204F Moscow *ELEKTROKHIMIYA* in Russian  
Vol 28 No 4, Apr 92 (manuscript received 25 Sep 91)  
pp 638-653

[Article by A.P. Karpinets and V.D. Bezuglyy; UDC 541.13]

[Abstract] Current trends in the development of the electrochemical synthesis of polymers, as well as recent progress in the study of the mechanism and kinetics of electrode processes involving different monomers at the cathode and anode were examined. The interconnection of the mechanism of electrochemical reactions and the route of homo- and copolymerization both directly on the electrode surface and in the bulk of the system is

substantiated. Recent publications devoted to the reactivity of electrochemical synthesis intermediates, i.e., free radicals, ion radicals, dianions, and dications, during direct and indirect initiation are discussed. Recent findings regarding the effect of the nature and physicochemical properties of the electrode, solvent, and background electrolyte on the individual stages of the electrochemical polymerization process are summarized. The following research areas were identified as being critical to further progress in electrochemical initiation of polymerization: 1) a detailed study of the topography and mechanism of the processes occurring during the electrochemical synthesis of polymers (specifically, identification of the sequence of reactions occurring on the electrode surface, in the double electrical layer, and in the bulk of the solution, etc.) and determination of the speed and role of each stage; 2) systematization and theoretical generalization of experimental data on the kinetics of the electrochemical synthesis process both on the electrode surface and in the bulk of the system, as well as identification of the optimal conditions for the directed synthesis of high-molecular compounds with specified properties; 3) a study of the phenomena occurring and the electrode-solution, electrode-polymer, and polymer-electrolyte interfaces to determine the role of the solvent and background electrolyte in the processes of electrochemical synthesis and modification of homo- and copolymers; and 4) discovery of the mechanism of the conduction and doping of electricity-conducting polymers in order to increase the efficiency of the electrochemical synthesis process. References 129: 39 Russian, 90 Western.

### The Electrochemical Destruction of Solid-Phase Polymers on a Cathode

927M0204G Moscow *ELEKTROKHIMIYA* in Russian  
Vol 28 No 4, Apr 92 (manuscript received 3 Jul 91)  
pp 654-668

[Article by A.A. Pud and G.S. Shapoval, Bioorganic Chemistry and Petrochemistry Institute, Ukraine Academy of Sciences, Kiev; UDC 541.138.3:547.322]

[Abstract] The electrochemical reduction destruction of polymers, while hard to classify as a basic branch of the electrochemistry of polymers, is directly linked to the problem of the stability of the polymeric materials used in electrochemical systems and may also prove to be a foundation for the development of research on the electrochemical modification and recycling of polymers. Research on the electrochemical reaction destruction of different classes of polymers in both dissolved and solid states indicates that the starting reaction of the process is the transfer of electrons to bonds, groups, or structures in macromolecules that are capable of electrochemical reduction. Two types of electrochemical reaction destruction of polymers exist—the accumulative and the dissociative types. The accumulative type of electrochemical reaction destruction is characteristic for polymers containing groups capable of forming rather stable

anion radicals, anions, and dianions. It entails the following principal stages: 1) transfer of electrons to the functional groups of the polymer followed by the formation of the respective anion radicals or dianions and accumulation of negative charges on the macromolecules; 2) redistribution of electron density in the reduced macromolecules and a change in their energies, bond angles, and lengths together with the occurrence of strong coulomb repulsion in the macromolecules between the charged fragments and between them and the negatively charged surface of the electrode; 3) decay of the reduced macromolecules; 4) transfer of their charged fragments to the catholyte; and 5) neutralization of the charged fragments by the solution's components and the moisture and oxygen in the air. The dissociative type of electrochemical reaction destruction is characteristic for polymers containing C-X bonds that split (dissociate) during reduction. It entails the following stages: 1) transfer of electrons to the macromolecule with synchronous splitting of the C-X bonds; 2) formation of conjugated and nonconjugated multiple bonds in the macromolecules; and 3) further reduction and transformation of the said macromolecules. The characteristics of these processes depend largely on the polymer's phase state. Both accumulative and dissociative electrochemical reaction destruction of polymers are discussed in detail. The review concludes with a brief section on the practical prospects regarding research on the electrochemical reaction destruction of polymers. Specifically, the copolymer of ethylene with vinyl acetate containing 12 vinyl acetate groups is said to be preferable to other ethylene + vinyl acetate copolymers in protective polymer coatings, and the possibility of using the capability of polytetrafluoroethylene and other perhalogen polyolefins to undergo electrochemical reduction in chemical current sources as an active cathode mass is said to be extremely interesting. Figures 5; references 67: 35 Russian, 32 Western.

**An Electrochemical and Roentgenographic Investigation of the Reversibility of a Lithium-Manganese Spinel in Lithium Chemical Current Sources With an Aprotic Electrolyte**

927M0205C Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 3, Mar 92 (manuscript received 7 Mar 91)  
pp 468-471

[Article by G.P. Yereiskaya, V.I. Yezikyan, O.N. Khodarev, B.P. Filimonov, and V.V. Ivanov, Novocherkassk Polytechnic Institute imeni S. Ordzhonikidze; UDC 541.138]

[Abstract] An electrochemical and roentgenographic study was conducted on the reversibility of a lithium-manganese spinel, i.e.,  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4(\text{Fd3m})$ , in lithium chemical current sources with an aprotic electrolyte in the voltage range from 2 to 3.7 V. Previous studies have established that the cathode reduction occurs in two stages and that the reversible redox processes occurring at the electrodes made of the study spinel are accompanied by a deformation phase transition of the first type that is close to the second type, i.e., Fd3m [to and from]

14<sub>1</sub>/amd. Analysis of the generalized phase diagram of the said spinel that was produced within the framework of the theory of deformation phase transitions has pointed to the possibility of yet another phase transition of the second type ( $14_1/\text{amd} \rightarrow \text{Fddd}$ ). In the study reported herein, the authors investigated the possibility of the formation of a rhombic spinel phase Fddd in the process of deep reduction of the electrodes from a cubic spinel and reversibility of the said process during cycling. The production of the lithium-manganese spinel and electrochemical and roentgenographic techniques used to study it have been described elsewhere. The cycling of the electrodes was conducted at a current density of 0.5 mA/cm<sup>2</sup> at voltages from 3.7 down to 1.0 V. The unit-area capacitance of the electrodes was found to depend on the composition, specific surface, and dimensions of the monocrystals, as well as on the end charge voltage. In coarsely dispersed spinels it is lower because of the incompleteness of the reduction of the particles. The discharge curves of the spinel  $\text{Li}_{1-x}\text{Mn}_2\text{O}_4$  were found to be steplike in nature. The roentgenographic studies of electrodes reduced to different voltages demonstrated a change in phase composition: In addition to a cubic spinel, there were reflections of a tetragonal  $\text{Li}_{1+y}\text{Mn}_2\text{O}_4$  ( $14_1/\text{amd}$ ) spinel phase and a rhombic ( $\text{Li}_{1+y+z}\text{Mn}_2\text{O}_4$  (Fddd) spinel phase. The researchers were thus able to develop an equation that qualitatively described the mechanism of the reduction of a lithium-manganese spinel in the range of voltages studied and to demonstrate the formation of a rhombic spinel phase that does not result in a decrease in electrodes' capacitance during cycling. Figures 3; references 6: 3 Russian, 3 Western.

**Production and Electrochemical Properties of Electrodes Modified by Polyethylene Imine Films**

927M0205D Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 3, Mar 92 (manuscript received 9 Jul 91)  
pp 473-477

[Article by M. Kkhaldun, Yu.M. Maksimov, and B.I. Podlovchenko, Moscow State University imeni M.V. Lomonosov; UDC 541.138]

[Abstract] The production and electrochemical properties of electrodes modified with cross-linked polyethylene imine films were studied. Modified polyethylene imines were studied by the method of cyclic voltammetry in 0.05 M  $\text{H}_2\text{SO}_4$ . Platinum electrodes in the form of plates (visible surface, 1.2 cm<sup>2</sup>) were used as working electrodes. Rotary-disk electrodes made of platinum (visible surface, 0.07 and 0.13 cm<sup>2</sup>) and glassy carbon (visible surface, 0.19 cm<sup>2</sup>) were also used. The electrodes' surfaces were modified by applying exact volumes of a polyethylene imine solution of specified concentration (1 to 5 wt-%) in isopropyl alcohol onto them. After the isopropyl alcohol was evaporated (by slight heating), a specified amount of dibromobutane dissolved in isopropyl alcohol was applied to the resultant film to cross-link the polymer. The electrode was then air-dried at 30-40° for an hour. The cross-linking was conducted at

temperatures of 80-90° for 35 to 40 hours as described elsewhere. The films studied had a degree of cross-linking of 0.5; polyethylene imine films with a thickness of  $8 \times 10^{-5}$  to  $2.5 \times 10^{-3}$  cm were used. The starting polyethylene imine had a molecular mass of 60,000. The moment the electrode was immersed in the  $K_3Fe(CN)_6 + H_2SO_4$  solution, there was a sharp growth in the peaks of the oxidation and reduction currents of the  $Fe(CN)_6^{3-/4-}$  ions. The potentials of the anode and cathode peaks coincided at the beginning of the saturation with redox anions. This was taken as confirmation of the fact that the electrode's potential during the course of the sweeping corresponds to a virtually equilibrium state of the ferro-ferricyanide system in the film. As the film becomes saturated with redox particles, a difference between the potentials of the anode and cathode peaks is noted that may be linked to an increase in the ohmic voltage drop as the polarization currents increase. In time, the film becomes fully saturated, and the current stops increasing (after 1 to 1.5 hours). The dependence of the formal diffusion coefficient of the charge on the concentration of ferricyanide particles in the polyethylene imine film was explained in terms of a model of charge transfer in the film. According to the said model, the charge is shifted in the film by the route of transfer of an electron between the comparatively low-mobility redox centers. The researchers hypothesized that charge transfer in the polyethylene imine films studied occurs primarily by the exchange of electrons between the redox particles fixed in the film and that physical diffusion of particles plays a much lesser role in the process. The saturation of the polyethylene imine films with ferricyanide anions was much more rapid when the electrode's potential was cycled than when the potential in the solution containing the study anions was kept practically constant. This finding was associated with reorganization of the electrostatic interaction of the anions with the polymer matrix as the particles' charge changed, as well as with a change in the distribution of the potential drop in the film when the potential was cycled. Figures 4; references 15: 3 Russian, 12 Western.

**An Electrochemical Investigation of the Systems Sodium Bromide-Water-n-Propanol and Sodium Iodide-Water-n-Propanol by the Method of the Electromotive Force of the Chains Without Transfer**

927M0205E Moscow *ELEKTROKHIMIYA* in Russian Vol 28 No 3, Mar 92 (manuscript received 7 Mar 91) p 478

[Article by T.I. Chankina, and V.I. Parfenyuk; UDC 541.135]

[Abstract] Solutions of sodium bromide and iodide in a mixed water and n-propanol solvent were subjected to electrochemical studies at a temperature of 298.15 K. Measurements were made of the electromotive force of the chains without transfer. The averaged ionic concentration coefficients of the activity of stoichiometric mixtures of sodium, bromine, and iodine ions were calculated, and the

primary effects of the medium in water-alcohol solvents were determined. References 3 (Russian).

**Volt-Ampere Electrode with Electrochemical Renewal of Mercury Film**

927M0211B Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Jul 92 pp 1289-1292

[Article by D. A. Khosroyeva, Ya. I. Turyan, N. K. Strizhov, Krasnodar Polytechnical Institute; UDC 543.253]

[Abstract] A mercury film electrode has an advantage over drop electrodes in terms of the utilization of toxic metallic mercury if the mercury film is formed and dissolved electrochemically in situ. This virtually avoids the need to work with metallic mercury. This article studies the use of such mercury film electrodes in voltammetry. The mercury film substrate was the end of a platinum wire 0.14 or 0.45 mm in diameter sealed in a glass tube and polished with the end of the glass tube. The Pt substrate provided good stability of the electrode material. The mercury film was applied from an electrolyte of  $Hg_2(NO_3)_2 + Ed(NO_3)_2 + HClO_4$ , the Cd(II) providing good adhesion of the mercury to the substrate. The electrochemical properties of the film electrode remained constant with mercury film thickness 10 to 25  $\mu m$ . Increasing Pt wire diameter causes a stronger edge effect, requiring an increase in film thickness. In studies performed over a period of time in automatic mode the limiting current for a given potential and concentration of metal ions were found to be proportional. The limiting current constants in the presence of complexants causing ligand-induced adsorption correlate with the stability of the complex ions involved. Figures 2; references 7: 6 Russian, 1 Western.

**Electrochemical Estimate of Free Gibbs Energy of Formation of Oxides As Functions of Stoichiometry**

927M0212F Moscow *NEORGANICHESKIYE MATERIALY* in Russian Jun 92 pp 1305-1308

[Article by N. A. Kipriyanov, I. G. Gorichev, I. S. Shaplygin, G. B. Rotmistrova, Moscow Commercial Institute; Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Russian Academy of Sciences; UDC 542.8]

[Abstract] Experimental determination of the free Gibbs energy of formation of nonstoichiometric metal oxides is based on the use of electrochemical methods, requiring high temperatures at which the oxides may not be stable. This work suggests the use of an electrochemical method for estimating the free Gibbs energy as a function of the stoichiometric composition, based on considering changes in the redox potential of manganese oxide with stoichiometric composition, pH and  $\ln a_{Mn}^{2+}$ . The method is based on the assumption that the potential-determining reaction at the oxide/

electrolyte interface is known. It is found that for nonhydrated manganese oxides the free Gibbs energy is approximated by an orthogonal Legendre polynomial. There is good correlation between free Gibbs energy and stoichiometric composition found by calculation using an equation (5) presented in the article

based on experimental data and the use of the interpolation expression presented in another equation (6). Electrochemical data are thus used to demonstrate that the free Gibbs energy of formation of metal oxides depends linearly on stoichiometric composition. Figure 1; references 13: 7 Russian, 6 Western.

**Removal of Ecologically Harmful Impurities from Air by Streamer Corona Discharge and UV Radiation**

927M0208B Moscow *KHIMIYA VYSOKIKH ENERGIY* in Russian Jul-Aug 92 pp 317-319

[Article by A. P. Shvedchikov, E. V. Belousova, A. V. Polyakova, A. Z. Ponizovskiy; UDC 541.15 542.7 628.5]

[Abstract] A study is presented of the possibility of improving the characteristics of the process of corona discharge purification of air with additives such as benzene Goncharov, styrene, xylene, phenol and acrylonitrile in moist air, using both pulsed and constant corona discharges in combination with UV irradiation. Studies were performed on a prototype laboratory installation including a gas-mixture preparation system, sources of corona discharge and UV radiation, a reaction chamber and a spectrophotometer. Maximum constant voltage of the corona discharge was 30 kV, maximum pulsed voltage 75 kV, pulse repetition frequency 2-50/s, pulse leading edge length 150 ns, pulse length 250 ns. Conversion was found to increase with increasing pulse repetition frequency, reaching a maximum of 95-98 percent. When the corona discharge was used with dry air, the reaction products contained only ozone its concentration little dependent on temperature between 20 and 70° C. Addition of UV radiation reduced the concentration of ozone. In moist air the rate of ozone decomposition was significantly higher, particularly at higher temperatures. The presence of organic additives also reduced the concentration of ozone to varying degrees, depending on concentration and chemical structure of the additive. The experimental data can be explained by a radical mechanism involving oxygen atoms and OH radicals generated by the corona discharge and photochemical decomposition of ozone. The combined use of corona discharge and UV radiation in moist air mixtures containing RH additives can convert the little-active  $O_3 + RH \rightarrow$  reaction products to a more effective channel with participation of O atoms and the OH radical, thus allowing more complete and rapid extraction of organic impurities from the exhaust gases of industrial enterprises. Figures 3; references 5: 4 Russian, 1 Western.

**Physical-Chemical Analysis of Industrial Wastes From Chemical Enterprises To Utilize Valuable Components**

927M0212D Moscow *NEORGANICHESKIYE MATERIALY* in Russian Jun 92 pp 1252-1254

[Article by D. A. Smagulova, M. S. Kazimbetova, M. R. Tanasheva, F. G. Suleymanova, N. A. Bektenov, Kazakh State University imeni S. M. Kirov; UDC 631.81.095.334(088.8)]

[Abstract] Methods of physical and chemical analysis are used to demonstrate possible means of utilizing valuable components from liquid and solid wastes. Considering that borogypsum consists primarily of calcium sulfate, an attempt was made to use it as an inorganic sorbent and to

study its sorption properties for phosphate ions. Experiments were performed by pouring a known quantity of phosphorous-containing waste water over a charge of borogypsum and agitating until equilibrium was reached. Process time was 15 minutes, S: = 1:200, pH 8-10,  $P_2O_5$  concentration in waste water 1420-3000 mg/dm<sup>3</sup>. The greatest influence on the process of ion exchange was found to be that of solution pH, which was adjusted by adding caustic soda. The addition of CaO to the sorbent was found to improve sorption properties of borogypsum, increasing  $P_2O_5$  in the solid phase to 26 mass percent. Similar experiments indicated that under optimal conditions with sorption of phosphate and borate ions up to 19.5-20.0 mass percent  $P_2O_5$  can be concentrated in the solid phase. An attempt was next made to solve the problem of purifying the wastes of "Kaustik" plant, which generates 18,000 tons of common salt contaminated with valuable and expensive amines, as well as calcium hypochlorite solutions. Methods of extraction and ion exchange were attempted. However, it was more effective to purify both types of waste solutions by treating them with each other. The amine-containing salt solutions and hypochlorite solutions were fed into a reactor and agitated for 5-10 minutes at a temperature between 25 and 70° C and the precipitate and purified water formed were analyzed. The method can be used to extract salt for use in various areas of the economy and calcite to be used as a construction material. Figures 4; references 7 Russian.

**Graphic Calculation of Process of Producing Chlorine-Free Potassium Fertilizer From Potassium Chloride and Ammonium Sulfate**

927M0212E Moscow *NEORGANICHESKIYE MATERIALY* in Russian Jun 92 pp 1258-1262

[Article by I. I. Goncharik, G. F. Pinayev, Kh. M. Aleksandrovich, Institute of General and Inorganic Chemistry, Belarus Academy of Sciences; UDC 632.83]

[Abstract] The influence of temperature and concentration of  $(NH_4)_2SO_4$  solutions used in the process of conversion of KCl and  $(NH_4)_2SO_4$  with various quantities of KCl on the interaction of KCl and  $(NH_4)_2SO_4$  with graphic analysis of the process was studied. For this purpose, areas of the solubility diagram of the salts were studied in the system K,  $NH_4Cl$ ,  $SO_4 \cdot H_2O$  at 20 and 75° C, the limits of crystallization of  $NH_4Cl$  and  $(K, NH_4)_2SO_4$ . Data on phase equilibria in the system were supplemented with experiments on the conversion of potassium chloride and ammonium sulfate formed at 20, 50 and 75° C, with  $(NH_4)_2SO_4$  concentration 30, 35, 40 mass percent, KCl consumption 80, 90 and 100 percent of stoichiometric. Utilization of the  $K^+$  and  $SO_4^{2-}$  ions increases with increasing concentration of initial ammonium sulfate solutions. This is also confirmed by the solubility diagram of the salts in the system studied, which shows that the greater the concentration of ammonium sulfate solutions used, the greater the length of the segment corresponding to the quantity of solid phase precipitated. Optimal conditions for conversion of KCl and ammonium sulfate are: T = 20° C, 35-40% ammonium sulfate solution and 100 percent KCl solution with respect to stoichiometry. Figures 2; references 2 Russian.

**Biochemical Purification of Effluent on Submerged Biofilter**

927M0213C Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 4, Apr 92 pp 212-213

[Article by V. I. Repkina, A. I. Mazyrina, V. S. Balakin; UDC 628:543.356]

[Abstract] Because of the wide spread of aniline in industrial effluent at many chemical factories, it was of interest to investigate the biochemical oxidation of aniline on submerged biofilters as a means of purifying the effluent of food and alcohol production plants. Biochemical oxidation was studied on a laboratory model using synthetic mixture representing the effluent. Starting with aniline concentration of 1 g/dm<sup>3</sup>, the purification process proved to be effective, removing aniline completely from the test sample. The pH of the solution increased during the test run due to the formation of ammonium nitrate. The purification of industrial effluent paralleled the experience gained in the laboratory setup. It was possible to lower aniline concentration down to 2.3 g/dm<sup>3</sup>, exceeding by 9-fold the maximum permissible concentration; this method appeared to be more effective than other bio-oxidation methods normally used for this purpose. Tables 2.

**Purification of Reversible Cycle Effluent of Petroleum Refining Plants From Mineral Impurities**

927M0231B Moscow *KHIMICHESKAYA PROMYSHLENNOST* in Russian No 4, Apr 92 pp 210-211

[Article by G. M. Beygeldrud, V. Ya. Vyazovik; UDC 628.543.665.6]

[Abstract] An electrochemical treatment of the reversible cycle effluent from a petroleum refining plant has been developed. In this paper an evaluation was reported of

this possible improvement in water processing methodology. This method is applied to water which has already passed through the pre-purification steps of petroleum catchment, sand traps and precipitation, just prior to the thermal evaporation. One of the problems at plant operations with circulating water system is the formation of solid scum in heat exchange pipes. The proposed method solves this problem by removing hard salts from the treated water, thus preventing their precipitation on the heating surfaces. It was shown that the pH of the effluent plays an important role in this process: at pH=9.6 overall hardness of the water can be lowered to 0.3 mg-eq/l. In this method pH is increased during the electrolysis step. The rate at which the electrode blocks dissolve in this operation determines how long this system can operate without a break. Four times a year the blocks need to be replaced. Table 1; figures 2; references: 5 (Russian).

**Ecologically Safe Varnish-Dyeing Materials for Furniture**

927M0232A Moscow *LAKOKRASOCHNYYE MATERIALY I IKH PRIMENENIYE* in Russian No 2, Mar-Apr 92 pp 10-18

[Article by V. G. Kireyeva; UDC 667.636.42'21.2]

[Abstract] In the developed countries furniture manufacturing represents one of the biggest users of varnish-dyeing products. The assortment of varnishes and dyes is quite diverse, with many specific compositions starting from the old nitrocellulose varnishes all the way to modern polyurethane and acrylic reagents. A pressure is always exerted by environment protective agencies limiting the content of volatile organic solvents and other toxic components. Extensive material was collected from many countries covering their products, applications, compositions, advantages and disadvantages. Considerable coverage was given to photo-setting varnishes, various additives counteracting the inhibitory action of oxygen, the use of UV illumination, water based varnish dyeing materials etc. Tables 6; references 62: 21 Russian (18 by Western authors), 41 Western.

**Polythermic and Isobaric Solubility Diagrams and Their Application to Mineral Fertilizer Technology**

927M0212C Moscow NEORGANICHESKIYE MATERIALY in Russian Jun 92 pp 1246-1251

[Article by L. N. Kaganskiy, I. M. Erayzer, T. I. Zaverityayeva, Odessa Polytechnical Institute; UDC 546.185]

[Abstract] Orthobaric solubility diagrams, their isothermic and polythermic cross sections are sufficient for the analysis of many chemical processes involving liquid and solid phases. However, when the vapor phase is also present, isobaric solubility results must be used to analyze the processes. The general form of isobaric cross sections of orthobaric solubility diagrams can be described by means of the rule of phases. The authors have previously described an improved visual-polythermic method and installation for the study of orthobaric solubility in complex systems, including when excess vapor pressure is formed over solutions. A new visual-polythermic method has also been developed to study isobaric solubility. This article describes the experiments involved, phase studies in a flask with reflux cooling, electric heating and magnetic agitation with moderate boiling to dissolve the salts present in the solution, either completely or partially dissolving the salts. If crystals remain with steady boiling, water is added by drops through the reflux cooler, the change in boiling point and dissolution of all crystals are observed. The composition of the saturated solution thus formed is determined by calculation. The isobaric cross sections of solubility diagrams are examined for the system  $\text{CaO-P}_2\text{O}_5\text{-H}_2\text{O}$  at a constant vapor tension equal to atmospheric pressure and in the area of formation of condensed phosphates. The process of high-temperature phosphoric acid decomposition of natural phosphates

and the process of drying of a superphosphate complex are analyzed by means of isothermic and isobaric cross sectional diagrams of the system. Other methods of drying superphosphate, in which the partial pressure of water is low, can also be analyzed by the same method. Figures 5; references 11 Russian.

**Compression of Granular Materials in Inorganic Salts and Mineral Fertilizers Technology. 4 Communication. Granulation of Fertilizers**

927M0213D Moscow KHIMICHESKAYA PROMYSHLENNOST in Russian No 4, Apr 92 pp 215-219

[Article by I. M. Kuvshinnikov, A. Ya. Tavrovskaya, N. Yu. Nikiforova; UDC 620.192.64:541.12]

[Abstract] This is a final paper of a series of papers devoted to theoretical considerations of fertilizer granulation; in it the authors have reported theoretical and experimental data on compression of various loose materials. Even though granulation is widely used in processing fertilizers, the scientific criteria for selection of a given granulation method have not been elaborated to date. The authors presented material showing that the widely accepted concept that fertilizer granulation mechanism is related to capillary compression of the liquid phase, could not be supported by experimental data. Development of the theory of compression of granular material leads to a concept about a directed structure formation of the fertilizers under the influence of adhesive forces caused by point surface defects of the crystalline lattice. Therefore, it is necessary to review the technological granulation procedures and design of granulation machinery in light of the mechanisms of the formation of adhesive and phase contacts of cohesion. Tables 3; figure 1; references: 10 (Russian).

### Fibers Based on Ceramic-Forming Polymers

927M0210A Moscow *KHIMICHESKIYE VOLOKNA*  
in Russian May-Jun 92 pp 4-11

[Article by A. M. Tsirlin, G. A. Budnitskiy, Z. F. Yegorushkina, State Scientific Research Institute of Chemistry and Technology of Heteroorganic Compounds, Moscow, All-Union Scientific Research Institute of Polymer Fibers, Mytishchi; UDC 677.014+547.281.261]

[Abstract] This review of the (primarily Western) literature discusses the status, properties, characteristics and prospects of silicon-carbide fibers, called "coreless" fibers. The first example of such a fiber is nikalon, manufactured by Dow Corning and Nippon Carbon. These fibers are intermediate in strength between fibers on substrates and carbon fibers, superior in heat resistance in oxidizing media to boron and carbon fibers, similar in properties to carbon fiber for reinforcement in composites, but 1.5-2 times more expensive. The fibers can be used to reinforce polymer, metal and ceramic matrices. The fiber is not simply an ultrafine heterogeneous mixture of SiC, SiO<sub>2</sub> and C, but a continuum consisting of alternating tetrahedrons of SiC<sub>4</sub> and SiC<sub>x</sub>O<sub>y</sub>, where x+y = 4. There is a thin film of SiO<sub>2</sub> on the surface. The heat conductivity and coefficient of thermal expansion are similar to those of SiC at 0 to 500 K. Electrical resistance is high. The fibers have high oxidation resistance and can be treated with hot acids and alkalis, do not react with metal powders at up to 900-1300 K and can be used in aluminum-matrix composites. Protective coatings are required for use with titanium. Silicon carbide fibers are brittle and strength characteristics must be computed statistically. They have high resistance to bombardment with fast neutrons and absorb microwave radiation well. The major means for increasing strength and modulus of elasticity is to reduce diameter, thus achieving more uniform structure and reducing defect content. The fibers are produced by dry formation from a melt of organosilicon polymers. An important advantage of metal composites made with these fibers is the slower loss of strength with increasing temperature than in the metals alone. Reinforcement of glass, glass ceramic and ceramic matrices is an important future area of application of these fibers. Increasing levels of future production will reduce the cost of these fibers to not over \$100 per kilogram. Figures 6; references 40: 8 Russian, 32 Western.

### Voltammetric Determination of Traces of Silver Using Graphite Electrode Modified by Sulfur-Containing Ligands

927M0211C Moscow *ZHURNAL ANALITICHESKOY KHIMII* in Russian Dec 91 pp 1297-1303

[Article by J. Labuda, M. Vanickova, V. V. Pavlishchuk, H. J. Holdt, Slovak Technical University, Bratislava, Czechoslovakia; UDC 543.25]

[Abstract] The purpose of this work was to present a systematic study of the influence of the structure of sulfur-containing macrocycles modifying a graphite electrode on the sensitivity and selectivity of determination of Ag<sup>+</sup> with and without competing complexants present in the solution. Voltammetric measurements were performed on a polarograph with a three-electrode cell. The working electrode was chemically modified graphite, the comparison electrode was saturated with a salt bridge preventing entry of the Cu<sup>+</sup> ion into the solution; the auxiliary electrode was a platinum wire. The analytic signal of Ag was found to increase in the sequence graphite electrode—graphite electrode coated with a film of naphion—electrode with the same film and ligand present on both the cathode and anode branches of the volt-ampere diagrams. Therefore, Ag<sup>+</sup> accumulates best of all on an electrode with a film containing a ligand, forming a three-dimensional complex cation bound by a sulfogroup in the naphion. The response of the electrode is proportional to the stability constant of the complex sorbed on the electrode. The range of concentrations which can be determined is 10<sup>-8</sup>-10<sup>-6</sup> mol/l Ag<sup>+</sup> with a standard deviation of 6 percent. Figures 4; references 10: 2 Russian, 8 Western.

### Interaction of Superconducting La-Sr Cuprate With Various Hydrothermal Solutions

927M0212A Moscow *NEORGANICHESKIYE MATERIALY* in Russian Jun 92 pp 1184-1189

[Article by E. N. Koritkova, N. I. Nesterchuk, L. N. Pivovarova, R. G. Grebenshchikov, Institute of Silicate Chemistry imeni I. V. Grebenshchikov, Russian Academy of Sciences; UDC 538.945]

[Abstract] Studies were performed on a superconducting oxide with the composition La<sub>1.8</sub>Sr<sub>0.2</sub>CuO<sub>4-δ</sub> (LSCO) synthesized by the ordinary ceramic method. Oxide specimens were exposed to hydrothermal media at 150-400° C and 10-70 MPa for 0.5-24 hr. Three series of experiments used water Grebenshchikov, aqueous alkali (NaOH and KOH) solutions and NaF solutions of various concentrations. At the pressure and temperatures used in the study water not only does not break down, but actually tends to stabilize the high temperature superconductor. The stabilizing effect apparently results from insertion of hydroxide ions formed upon disassociation of the water into the vacant oxygen positions of the cuprate. Increases in pressure and time favor, in temperature tend to negate the stabilizing effect. In alkaline solutions, exposure over 1 hour has a negative influence. In sodium fluoride was found to be most effective in preventing corrosion of the oxide due to insertion of F ions into the crystalline structure of the cuprate. Figures 4; references 6: 3 Russian, 3 Western.



**New Compounds in Systems  $\text{Ln}_2\text{O}_3\text{-BaO-Fe}_2\text{O}_{3+\delta}$**   
927M0212B Moscow NEORGANICHESKIYE  
MATERIALY in Russian Jun 92 pp 1197-1201

[Article by D. A. Kudryavtsev, B. V. Mill, N. F. Vedernikov, I. S. Shapligin, Institute of General and Inorganic Chemistry imeni N. S. Kurnakov, Russian Academy of Sciences; Moscow State University imeni M. V. Lomonosov; UDC 546.431.654.621]

[Abstract] New compounds of  $\text{LnBa}_3\text{Fe}_2\text{O}_{7.5+\delta}$  ( $\text{Ln} = \text{La}, \dots, \text{Lu}, \text{Y}$ ) have been synthesized by the authors. The compounds  $\text{LnBa}_3\text{Fe}_2\text{O}_{7.5}$  were prepared by solid-phase synthesis in air at 1100-1500° C from  $\text{Ln}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{Fe}_2\text{O}_3$ . The compounds  $\text{LnBa}_3\text{Fe}_2\text{O}_{7.5+\delta}$  with  $\text{Ln} = \text{La}, \text{Hf}, \text{Er}, \text{Tm}$  are unstable in air. They absorb moisture and carbon dioxide and degrade, changing color. The compounds  $\text{LnBa}_3\text{Fe}_2\text{O}_{7.5+\delta}$  crystallize in four structural types depending on the dimensions of  $\text{Ln}^{3+}$ : where  $\text{Ln} = \text{La}, \dots, \text{Nd}$  they are hexagonal; where  $\text{Ln} = \text{Sm}, \dots, \text{Gd}$  they are differentiated in a monoclinic system; where  $\text{Ln} = \text{Dy}, \dots, \text{Tm}, \text{Y}$  they are isostructural with rhombic  $\text{YBa}_3\text{Al}_2\text{O}_{7.5}$ , but have no monoclinic modification; where  $\text{Ln} = \text{Er}, \dots, \text{Lu}, \text{Tb}$  they have the structure of cubic perovskite. Low-temperature magnetic susceptibility anomalies have been detected in these new compounds, corresponding to the transition to the magnetically ordered state. Below  $T_N$  the compounds are antiferromagnetic.  $T_N$  falls in the interval of 7-21 K. Figure 1; references 8: 3 Russian, 5 Western.

**Influence of Electrochemical Processes on Reflection of Ultrasound Impulse From "Electrolyte Solution-Metal" Separation Border**

927M0232A Kiev FIZIKO-KHIMICHESKAYA  
MEKHANIKA MATERIALOV in Ukrainian  
Vol 27 No 4, Jul-Aug 91 (manuscript received  
10 Aug 90) pp 124-125

[Article by V. F. Kondrat, S. O. Lyzun, D. N. Lyashchuk, Institute of Geology and Geochemistry of Fossil Fuel, Academy of Sciences of Ukraine, Lviv; UDC 541.138.541.135.52:534.24]

[Abstract] Ultrasound vibrations may have considerable effect on the course of electrochemical processes at the border between metal contact and electrolyte solution. Conversely, the electro-chemical processes may have an effect on the reflection of high frequency ultrasound waves. This situation was investigated on a specially constructed equipment. Aluminum, iron and copper electrodes were tested. In some cases the reflected impulse exceeded the initial value; otherwise there was either no effect on the reflected impulse or it gradually dissipated to zero. The decrease may be due to presence of gas bubbles on the surface of the electrodes which act as diffusing agents for the ultrasound waves. The phenomenon of increased values for the reflected impulse remains unsolved. Figures 3; reference 2: (Russian).

**Photoelectronic Spectra of Trialkyl Phosphates**

927M0239A Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 25 Mar 91) pp 570-576

[Article by B.V. Okhota, V.I. Vovna, L.N. Alekseyko, Yu.V. Prikhodko and D.V. Yudin, Scientific Research Physicochemical Institute, Far Eastern State University, Vladivostok; UDC 546.1.118:539.194]

[Abstract] Tabulated data are presented on the photoelectronic spectra of trialkyl phosphates,  $(RO)_3PO$ , where  $R = CH_3, C_2H_5, C_3H_7, C_4H_9, C_{5H_{11}}$  and  $C_6H_{13}$ . Data interpretation was based on the high degree of correlation ( $\geq .98$ ) with  $n^H$ -orbitals of relatively simple alkyl alcohols, ROH, and with  $\sigma$  constants. The alcohols selected for comparison ranged from methanol to 1-heptanol, since the trialkyl phosphates retain the group orbitals of alkyl alcohols. Mathematical analysis revealed the first 5 ionization potentials, with the first 3 bands in the entire spectrum attributed to oxygen orbitals. Increasing complexity of the R group blurred differences between the 2nd and the 3rd ionization potentials, but even in the case of the  $C_6H_{13}$  group the difference was on the order of 0.3 to 0.4 eV. Figures 2; tables 4; references 20: 9 Russian, 11 Western.

**Synthesis of P-Containing 3-(2,2-Dichlorovinyl)-2,2-Dimethylcyclopropanecarboxylic Acid Esters**

927M0239B Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 14 May 91) pp 583-588

[Article by V.V. Kormachev, O.A. Kolyamshin, Yu.N. Mitrasov and Ye.A. Anisimova, Chuvash State University imeni I.N. Ulyanov, Cheboksary; UDC 547.341+547.512]

[Abstract] Novel 3-(2,2-Dichlorovinyl)-2,2-dimethylcyclopropanecarboxylic acid esters were synthesized as part of a screening program for insecticides. The esters were synthesized by a series of reactions commencing with the reaction of dialkyl phosphites with 2,2-dichlorocyclopropanecarbaldehyde in the presence of sodium methylate in methanol to give dialkyl-1-(2,2-dichlorocyclopropyl)-1-oxymethylphosphonates. The next stage involved reaction of 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxyl chloride with dialkyl-1-alkyl(aryl)-1-oxymethylphosphonates in toluene catalyzed by pyridine or triethylamine to give the target esters. Tables 5; references 5: 3 Russian, 2 Western.

**Phosphorylated Adamantanes. Part 13. Chemical Shifts in 1-R-Adamantyl-3-Dichlorophosphonates**

927M0239C Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 28 Aug 90) pp 589-592

[Article by R.I. Yurchenko, O.M. Voytsekhovskaya, I.N. Verpovskaya and A.A. Kudryavtsev, Institute of Surface Chemistry, Ukrainian Academy of Sciences, Kiev; UDC 547.678+547.421]

[Abstract] Impact of 1,3-substituents in adamantane on chemical shifts was assessed by means of PMR,  $^{31}NMR$  and IR spectroscopies. Spectroscopy of 1-R-adamantyl-3-dichlorophosphonates, where  $R = H, Br, ONO_2, POCl_2, NCHOCH_3, Me, Et, CN, COOH, COOMe$ , etc., demonstrated the fact that inductive effects of the substituents affected signal shifts of central and bridge protons. In addition, a direct correlation prevailed between the degree of chemical shift and inductive strength of the substituent group. The presence of electrophilic substituents attenuated electron donor characteristics of phosphoryl oxygen and facilitates nucleophilic substitution of Cl atoms on the diphosphoryl group. Tables 1; references 15: 13 Russian, 2 Western.

**Catalytic Properties of Organic Bases in Synthesis of P-Containing Thiosemicarbazides**

927M0239D Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 21 Oct 91) pp 606-610

[Article by N.I. Yanchuk, Ternopil State Pedagogical Institute imeni Ya.A. Galan; UDC 547.234.1+547.241+541.128]

[Abstract] Screening studies were conducted on the efficiency of selected organic bases in promoting synthesis of P-containing thiosemicarbazides. Kinetic monitoring of the reaction of diphenylphosphonate hydrazide with phenylisothiocyanate at 25° C in benzene catalyzed by N- and O-containing organic bases showed that efficiency of the catalysts was directly correlated with their capacity for hydrogen bond formation ( $pK_{HB}$ ). The results demonstrated a direct correlation between ( $pK_{HB}$ ) and reaction rate enhancement. In terms of efficiency, the following ranking was derived for the different classes of the organic bases: nitriles < esters = carboxylic acid esters < phosphoric acid esters < carboxylic acid amides < sulfoxides < phosphin oxides. The common underlying catalytic mechanisms appears to be rapid formation of a N-H...B-linked activated complex with diphenylphosphonate hydrazide and its subsequent reaction with the isothiocyanate and regeneration of the catalyst. Tables 2; references 12: 10 Russian, 2 Western.

**Reaction of Ester Amides and P(III) Acid Amides With A-Chloraldehydes**

927M0239E Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 23 Jan 90) pp 611-616

[Article by I.A. Aleksandrova, L.K. Salkeyeva, Yu.V. Chugunov and T.Kh. Gazizov, Karaganda State University; Institute of Organic and Physical Chemistry imeni A.Ye. Arbuzov, Kazan Scientific Center, Russian Academy of Sciences; UDC 547.16'118+547.446.1]

[Abstract] Studies on reactions of ester amides and P(III) acid amides with  $\alpha$ -chloraldehydes revealed different solvent-dependent mechanisms and pathways. Reaction of tert-butyl(tetraethyldiamido)phosphite (I) with trichloroacetaldehyde followed 2 pathways leading to tetraethyldiamidochlorophosphate (II) and  $\beta,\beta$ -dichlorovinyl(tetraethyldiamido)phosphate (III). In petroleum ether, methylene chloride and aqueous solvent the ratios of products II and III were as follows: 4:5, 3:2 and 9:1, respectively. Compound I reacted with mono- and dichloroacetaldehyde to give II, vinyl(tetraethyldiamido)- and  $\beta$ -chlorovinyl(tetraethyldiamido)phosphate. These observations demonstrated that product formation was dependent on the number of Cl atoms in the aldehyde and the degree of positive polarization of one of these atoms. The initial steps involve reaction of the phosphite P atom with the polarized Cl atom Tables 1; references 12: 9 Russian, 3 Western.

#### Synthesis and Reactivity of P- and N-Congeners of 5,6-Benzocoumarin

927M0239F Moscow ZHURNAL OBSHCHEY KHIMII in Russian Vol 62 No 3, Mar 92 (manuscript received 22 Feb 91) pp 661-667

[Article by O.V. Skripskaya, P.I. Yagodinets, I.N. Chernyuk and M.I. Shevchul (dec), Chernivtsi State

University imeni Yu. Fedkovich; UDC 547.587.51:661.718.1:547.7/8:543.422]

[Abstract] Interest in novel fluorescent compounds led to studies on the synthesis and properties of P- and N-congeners of 5,6-benzocoumarin. Reaction of 3-( $\omega$ -bromoacetyl)-5,6-benzocoumarin in nucleophilic substitution reactions with triphenylphosphine yielded 5,6-benzocoumarin-3-yl-carbomethyltriphenylphosphonium bromide (II). Treatment of II with potash led to dehydrobromination with formation of 5,6-benzocoumarin-3-yl-carbomethylenetriphenylphosphorylide (III). 5,6-benzocoumarin-derivatized unsaturated ketones were obtained by reaction of III with various aldehydes in boiling toluene. Finally, reaction of III with Br<sub>2</sub> resulted in conversion to the  $\alpha$ -brominated salt; treatment of the latter with potash led to elimination of HBr and yielded  $\alpha$ -Br substituted phosphorylide. Heating of the phosphorylide with methyl iodide and p-nitrobenzylbromide resulted in C-alkylation, while reaction with ethyl iodide yielded O-alkylation. In addition, a number of heterocyclic compounds were synthesized by the reaction of 3-bromoacetyl-5,6-benzocoumarin with thioacetamide, 2-aminothiazole, 2-aminopyridine, 6-aminopurine and o-phenylenediamine. Tables 3; references 6: Russian.

**An Electrode Based on a Copolymer of Aniline and p-Aminophenol With a Phenol Function**

927M0201B Moscow ELEKTROKHIMIYA in Russian  
Vol 28 No 2, Feb 92 (manuscript received 2 Aug 90;  
after revision 26 Jun 91) pp 181-189

[Article by I.A. Vinokurov, S.Ya. Khaykin, V.V. Bertsev, and T.M. Karkhu, Leningrad State University; UDC 541.134]

[Abstract] An electrode based on a copolymer of aniline and p-aminophenol with a potentiometric sensor was developed to respond to a change in the concentration of molecular phenol in neutral aqueous media (a phosphate buffer with a pH of 7). The electrode, which was coated with a polymer film, was prepared by electrochemical synthesis at a constant potential of 2.5 V for 100 seconds on a platinum wire (with a surface area of 0.2 cm<sup>2</sup>) from a solution of 0.1 M C<sub>6</sub>H<sub>5</sub>NH<sub>2</sub> + 0.2 M p-C<sub>4</sub>H<sub>4</sub>(OH)NH<sub>2</sub> + 1 M LiClO<sub>4</sub> in acetonitrile. The polymer coating was a greenish brown. A PI-50-1.1 potentiostat with a PR-8 programmer, a V 3-21 voltmeter, and a PH-262 pH-meter were used during the course of the research. Infrared spectra were recorded, and the structural fragments of the newly synthesized copolymer were analyzed. The researchers then proceeded to propose a scheme for a potential-determining electrode process involving fragments of polymer chains and molecular phenol. They substantiated the possibility of using Nikolskiy-type equations for electrodes of the type under consideration and determined the conditions under which the equations would be applicable. Next, the researchers studied the dependences of the potential of an electrode that was not polarized by an external current on the concentration of phenol in aqueous buffer solutions. A correlation (0.81) was established between the coefficients of the electrode selectivity of such a sensor with respect to phenol and the potentials of the peaks of irreversible oxidation of the phenols as determined from potentiodynamic curves. The authors concluded by hypothesizing that the interconnection between selectivity coefficients and electrochemical oxidation process parameters is common to the entire class of sensors based on electricity-conducting organic polymers with conjugated bonds. Figures 3; references 16: 6 Russian, 10 Western.

**Intensification of Graft Polymerization in Modification of Polycapraamide Fibers**

927M0210B Moscow KHIMICHESKIYE VOLOKNA  
in Russian May-Jun 92 pp 11-12

[Article by V. G. Zaikov, T. V. Druzhinina, L. S. Galbraykh, Moscow Textile Academy; UDC 677.494.675]

[Abstract] Existing methods of producing grafts in polycapraamide and polydimethylaminoethylmethacrylate graft copolymers are either inefficient or complicated by the need to use a redox component in the synthesis or fiber formation stage. This article reports on studies

intended to develop new, more effective initiating systems allowing the reaction of graft polymerization to be performed before the monomer has undergone hydrolysis, thus increasing the degree of monomer utilization. This was achieved by the use of Cu<sub>k</sub><sup>2+</sup> - H<sub>2</sub>O<sub>2</sub> to initiate the process. Kinetic curves indicate that greater activity is achieved in this manner by changing the oxidation-reduction potential of Cu<sup>+</sup> - Cu<sup>2+</sup> during complex formation. Figures 2; references 4 Russian.

**Influence of Twist on Composite Strengthening of Complex Hard-Chain Polymer Filaments**

927M0210C Moscow KHIMICHESKIYE VOLOKNA  
in Russian May-Jun 92 pp 22-24

[Article by M. P. Nosov, N. I. Vagin, V. A. Smirnova, T. I. Kozhemyaka, V. I. Pirogov, Kiev Affiliate, All-Union Scientific Research Institute of Polymer Fibers; UDC 677.017.33+539.383.2]

[Abstract] A study was made of the effect of composite hardening of fibers of rigid-chain polymers by both twisting and saturating with binders. Studies were performed on various filaments in two stages. The first stage studied the influence of twisting on filament strength; the second stage studied the combined influence of twisting and saturation with polyurethane semicarbazide. Saturation with binder was found to shift the maximum on the strength vs twisting curves into the area of lower amounts of twisting and into the area of higher rupture stress. Composite strengthening as a result of binder saturation along with no twisting yielded strength increases of 18-100 percent for various fibers. The maximum composite strengthening by both twisting and saturation was equal to the difference in strength of saturated and unsaturated fibers at the critical amount of twisting. The strength increase was 28-46 percent. Overall increases by the use of both methods was 70-170 percent for the same fibers. Fibers twisted to other than the optimal amount might actually become weaker following saturation with binder. It is thought that the additional composite hardening resulting from saturation of properly twisted fibers is achieved by changing the nature of failure of element refilaments in the direction of multiple fractures. Twisting itself results in failure by multiple fractures. Figure 1; references 14: 13 Russian, 1 Western.

**Use of Plasma Treatment to Improve Adhesive Properties of Polymer Materials**

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[Article by I. N. Brovikova, V. L. Abramov, S. D. Menagarishvili, Ivanovo Institute of Chemical Technology; UDC 621.382.537.525]

[Abstract] Treatment in a low-temperature gas-discharge plasma is a promising method of modifying polymer materials, acting only on the surface layer of the material

down to a few  $\mu\text{m}$  or less. The authors have performed studies to determine the possibility of producing metalized films of PVC with satisfactory adhesive properties by magnetron atomization of stainless steel, coating thickness 0.1  $\mu\text{m}$ . A glow discharge was used to treat plasticized PVC films in the magnetron atomizer at 13.3 Pa and a current of 100 mA. The results indicated that a 5 or 10 minute treatment was sufficient to reduce the quantity of free plasticizer extracted from PVC films by one or two orders of magnitude. The mass loss due to etching of the polymer in the oxygen plasma is not over 0.5 percent. Virtually no changes in physical properties were observed. The plasticized PVC films were coated with stainless steel after treatment with the glow discharge by atomization of the metal in argon for 20 minutes and the adhesive strength of the coating was compared with that achieved on untreated plastic. Preliminary processing in the oxygen plasma did not change the reflectivity of the coating but did increase the bonding strength of the metal with the polymer surface by about 3-5 times. Figure 1; references 2 Russian.

**Structure and Properties of Composite and Ultrathin Fibers of Polymer Mixture Melts**

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[Article by N. M. Rezanova, M. V. Tsebrenko, Kiev Engineering Institute of Light Industry; UDC 677.494.014.578]

[Abstract] The authors studied the structure and properties of fibers formed from melts of mixtures of polymers with specific interaction of the components at the phase interface as a function of conditions of deformation of the melt and properties of the initial polymers. The objects studied were mixtures of ethylene polymer with vinyl acetate and copolyamide. Two specimens of ethylene-vinyl acetate copolymer were studied, manufactured in Kazan and in Germany. Fibers were produced on a laboratory spinning machine in a field of longitudinal speed gradient. Complex filaments were produced by extracting the matrix polymer with a solvent. The CEVA and CPA were found to have different capacities for longitudinal deformation, CPA deforming much better in a tensile force field. Mixtures produced by extrusion containing 20-40 percent CEVA did not have fiber-forming properties. This seems to result from the formation of large numbers of hydrogen bonds between the CEVA and CPA macromolecules. When CPA is added to CEVA the CEVA is reinforced by CPA microfibers but the strength does not achieve additive values. Addition of CEVA to CPA causes a decrease in the strength of monofilaments even below the additive values. The deformation properties of ultrathin CEVA fibers formed from CEVA-CPA mixtures are similar to the properties of polyurethane spandex fibers, but the process is simpler and more ecologically benign. Figure 1; references 5 Russian.

**Gamma Radiolysis of Benzosubstituted Crown Ethers**

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[Article by Ye. I. Grigoryev, S. V. Nesterov, O. V. Mikhailitsyna, L. I. Trakhtenberg, T. G. Myasoyedova; UDC 541.15]

[Abstract] A study is presented of the mechanism of radiolysis and radiation stability of benzo- and dibenzo-substituted crown ethers in the solid phase as a function of the dimensions of the polyether ring and the presence of alkyl substituents. Specimens in a vacuum of  $10^{-3}$  Pa were irradiated at 77 K with 2 and 20 Gr/s from  $^{60}\text{Co}$ . EPR spectra were recorded at 77-300 K. Mass spectra were recorded. The results obtained indicate that the primary process in radiolysis of crown ethers with benzene substituents in the polyether ring is breaking of the C-O macrocycle. The major process is breaking of the ether bond between a  $\text{CH}_2$  group and the nearest oxygen atom to the benzene ring with subsequent elimination of one or more  $-\text{CH}_2-\text{CH}_2-\text{O}-$  structural units. Separation of H atoms from  $-\text{CH}_2-$  groups in the polyether ring is less probable. Breaking of C-C bonds is improbable. The presence of methane, ethylene and traces of CO indicate that further fragmentation occurs in the solid phase. The effectiveness of fragmentation of crown ethers in the solid phase is greatly reduced by the cell effect, which causes rapid deactivation of excitation. References 17: 5 Russian, 12 Western.

**Spectral and Kinetic Characteristics of Radiation Defects in  $\text{NaNO}_3$ - $\text{NO}_2^-$  Crystals**

927M0208C Moscow *KHIMIYA VYSOKIKH ENERGIY in Russian Jul-Aug 92 pp 320-323*

[Article by V. S. Dolganov; UDC 541.15]

[Abstract] Earlier works have shown that isovalent cation and anion impurities introduced to nitrates of sodium and potassium are effective hole acceptors. This work uses high-speed optical spectroscopy to study the spectral and kinetic parameters of the processes of birth and death of activator and matrix centers in  $\text{NaNO}_3$ - $\text{NO}_2^-$  crystals and studies the temperature and concentration dependence of center-formation effectiveness. Nitrite ions were introduced to a nitrate matrix by cocrystallization by slow cooling of saturated aqueous solutions of the corresponding salts with molar activator content 0.1-5 percent. Measurements were performed on a pulse radiolysis installation. The radiation source was a high-current electron pulse accelerator with pulse length 18 ns, pulse current up to 2 kA, mean electron energy 200 keV. Specimens were held in a cryostat with residual pressure not over 0.1 Pa. It was found that increasing concentration of  $\text{NO}_2^-$  negative ions decreased the yield of the  $\text{NO}_3^0$  radicals, probably due to the competitive hole-capture reaction of the impurity ions and increased the yield of another matrix center—the

peroxynitrite ( $\text{OONO}^0$ ) as a result of extinguishing of excited states of  $\text{NO}_3$  by the nitrite ions, annealing the peroxynitrite. The method of high-speed optical spectroscopy was found to be effective in measuring the kinetic characteristics of birth and death of the products of radiolysis of sodium nitrate crystals doped with nitrite ions over a broad temperature interval. Figures 2; references 12 Russian.

**Purification of Air of  $\text{SO}_2$  and  $\text{NH}_3$  Impurities with Constant Corona Discharge and UV Radiation**

927M0208E Moscow *KHIMIYA VYSOKIKH ENERGIY in Russian Jul-Aug 92 pp 377-378*

[Article by A. P. Shvedchikov, E. V. Belousova, A. V. Polyakova, A. Z. Ponizovskiy, V. A. Goncharov; UDC 541.15;542.7 628.5]

[Abstract] A study was made of the possibility of increasing the slow rate of removal of  $\text{SO}_2$  and  $\text{NH}_3$  from polluted air by the combined effect of a constant corona discharge and UV radiation. Experiments were performed on a flow-through installation with a 1.3 liter reaction chamber containing a medium-pressure mercury UV lamp at a distance of 70 mm from the corona electrode. Products were identified by spectrophotometry. It was found that the constant corona discharge alone yielded an increasing concentration of ozone and conversion of  $\text{SO}_2$  and  $\text{NH}_3$  with increasing voltage, but the absolute values of conversion were small, about 15 percent for  $\text{NH}_3$  and 30 percent for  $\text{SO}_2$  at 25 kV. Addition of UV radiation significantly improved the results, the conversion increasing to 80-90 percent for both pollutants with a simultaneous reduction of ozone at the output of the reaction chamber by about 2.5 times. The UV radiation initiates photochemical reactions which combine with the radiation-chemical reactions, utilizing various active intermediate particles. This increases the rate of  $\text{SO}_2$  oxidation. The increased rate of  $\text{NH}_3$  breakdown is apparently related basically to the breakdown of ozone and oxidation of  $\text{NH}_3$  by active oxygen atoms and hydroxyl radicals. Figure 1; references 5: 4 Russian, 1 Western.

**Radiation-Chemical Formation of Acid in Films of Polyvinylbutyral with Chlorine-Containing Additive**

927M0208F Moscow *KHIMIYA VYSOKIKH ENERGIY in Russian Jul-Aug 92 pp 379-380*

[Article by Z. K. Kriminskaya; UDC 541.15]

[Abstract] The radiation-chemical yield of acid was measured in polyvinylbutyral films containing chloralhydrate and hexachloroethane. Films were formed of a mixture of PVB, chloralhydrate recrystallized from ethyl alcohol, hexachloroethane and absolute alcohol dried at room temperature for 1 day. The film was then cut into rectangles and irradiated on a  $^{60}\text{Co}$  gamma

installation at 1.5 Gr/s. A spectrophotometer was used to measure the optical density of the PVB films. Gamma irradiation changed the color of the film from yellow to red, indicating the formation of acid. A calibration graph was used to produce quantitative characteristics of the process. It was found that for

large chloralhydrate concentrations the acid yield increased with dose, for lower concentrations it decreased with increasing dose. Hexachloroethane caused the same color change, but the acid yield decreased with increasing gamma radiation dose. Figure 1; references 5: 1 Russian, 4 Western.

**Antistatic Coatings**

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MATERIALY I IKH PRIMENENIYE in Russian  
No 2, Mar-Apr 92 pp 22-31

[Article by O. F. Aleksashina, V. G. Shigorin; UDC  
(047)667.613:677.044.333.1'42.2]

[Abstract] Antistatic coatings are widely used in current electronic, biological, medical, food and other technologies. Static electric charges are initiated on the surface of dielectrics upon rubbing and/or skidding. Most varnish-dyeing materials are such dielectrics. The get rid of static electricity, it is necessary to remove it via surface or volume conductivity or by dissipation into the surrounding atmosphere. In this paper, a literature review has been presented on various aspects of antistatic varnish-dyeing coatings ( $P_k$ ). Most electricity conducting and antistatic  $P_k$  are composite materials containing metal and carbon fillers. Specific agents used to provide antistatic properties were discussed, their selection usually being based on the desired end-effect of the coating. For example, to increase thermal and wear resistance of  $P_k$ , copper powder modified with titanium organic compounds is used; effective electric conductivity, anticorrosive properties and durable service is obtained by adding copper and tin. Transparent antistatic  $P_k$  products can be obtained by introducing trioxide with small quantity of antimony, etc. Many other specific applications and modifications were discussed. References 139: 128 Russian (111 by Western authors), 11 Western.

**Evaporation of Fire Hazard Solvents During  
Drying of Electro- Insulating Coatings Under  
Non-Stationary Temperature Conditions**

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MATERIALY I IKH PRIMENENIYE in Russian  
No 2, Mar-Apr 92 pp 45-48

[Article by A. Ya. Voloshchuk, Yu. A. Koshmarov, V. V. Andreyev, Higher Engineering Fire-Technical School; UDC 614.841.45:6667.641'645]

[Abstract] Drying technical electric articles covered with varnish or enamel requires heating them in convection-radiation kilns to the temperature of varnish polymerization. This is a non-stationary process, the course of which depends on the source of heat and on the geometric and thermophysical parameters of the heated object. Based on theoretical considerations and experimental studies, a differential equation was derived making it possible to determine the intensity of evaporation of fire hazard solvents from electro-insulating varnish-dyeing materials under non-stationary temperature conditions. It could be used in calculation of fire and explosion safe working conditions and for ventilation of drying kilns used with such products. Figures 5; references 5: 4 Russian, 1 Western.